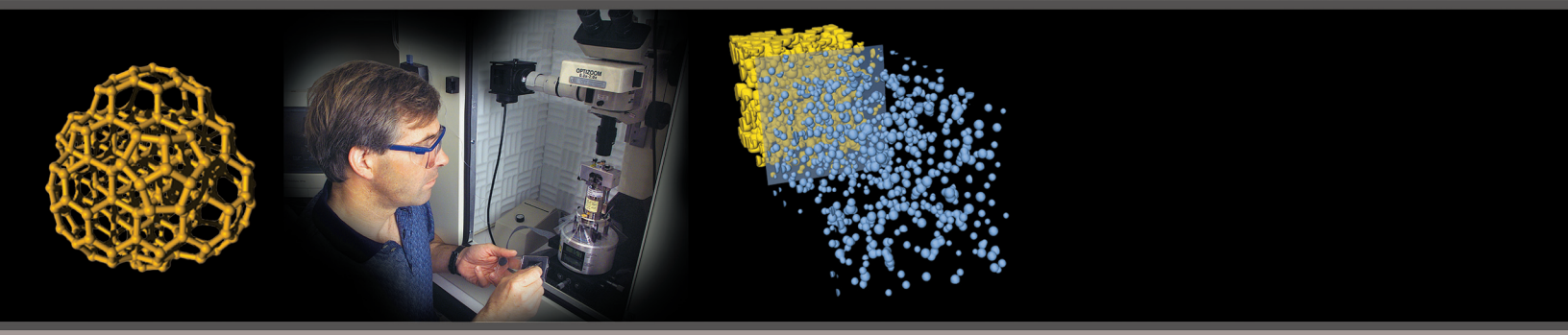
Chemistry & Materials Science

Lawrence Livermore National Laboratory



Annual Report 2002

chemistry & materials science
CMS

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Message from Tomas Diaz de la Rubia

From the earliest days of the Lawrence Livermore National Laboratory (LLNL), the Chemistry and Materials Science (CMS) Directorate has provided scientific and technical leadership to the Laboratory, thus helping LLNL fulfill its mission of national security. Over the years, CMS has been renamed and reorganized several times, and its facilities and programs have been modified and expanded to meet the Laboratory's changing needs. However, the directorate's common theme and determination to "do great science" have remained constant.

Historically, CMS has successfully confronted some of Livermore's toughest scientific and technological challenges by recruiting and retaining outstanding multidisciplinary talent. Today, as in the past, we are charged with extraordinary responsibilities in an environment of continuous change. We have been called to execute and support the Laboratory's most important programs in national security, homeland security, energy, environment, and health, as well as fundamental research inspired by these program areas. Our staff understands the magnitude and importance of these programmatic missions and is tackling the many facets of each challenge by conducting cutting-edge research that pushes forward on scientific frontiers.

For example, new scientific fields are being created at the interfaces of conventional disciplines—biology, chemistry, and materials science; nanoscience and nanotechnology; and laser–materials interactions. In addition, present-day terrorist tactics using nuclear, chemical, and biological weapons have increased the urgency of scientific and technical discoveries in forensic science. At the same time, there is a growing need in all these research areas for large-scale simulation and computing using resources from the Advanced Simulation and Computing (ASCI) Program.

With a high-quality workforce and a state-of-the-art scientific and technical infrastructure, our directorate is prepared to take advantage of the opportunities offered by these new frontiers so that we can accomplish our mission of supporting the Laboratory through excellence in the chemical and materials sciences. To fully realize our vision of being the premier provider of scientific leadership in support of Laboratory programs, we must meet and anticipate changes in programmatic needs through innovations in science and technology. We must also continue to provide an exceptional and safe work environment that attracts and retains a vital and diverse workforce.

As the new associate director of CMS, I have chartered a team of senior leaders to initiate a strategic-planning project to address these challenges. The team has identified four research themes that define our directorate's work and that unite our staff in a set of common goals:

- Materials properties and performance under extreme conditions
- Chemistry under extreme conditions and chemical engineering in support of national-security programs
- Science in support of national objectives at the intersection of chemistry, materials science, and biology
- Applied nuclear science for human health and national security

This Annual Report, the first in its series, is organized to represent the culture of our directorate—state-of-the-art science and technology; a dynamic organizational structure; and a staff that honors our mission and vision with prestigious awards, worldwide recognition, and outstanding publications.

The science and technology section addresses challenges, achievements, and new frontiers within each of the four research themes:

- **Materials properties and performance under extreme conditions**—investigations of the properties and performance of metals (e.g., plutonium, tantalum, copper, iron, and tin) under extreme conditions of shock, pressure, stress, temperature, and strain rate, as well as studies of quantum-confinement and surface-passivation effects in nanomaterials.

- **Chemistry under extreme conditions and chemical engineering in support of national-security programs**—insights into the chemical reactions of energetic materials in the nuclear stockpile through models of molecular response to extreme conditions (e.g., quantum effects in chemical systems and energetic-material response during detonation) and a new technique for processing energetic materials by using sol-gel chemistry.

- **Science in support of national objectives at the intersection of chemistry, materials science, and biology**—multidisciplinary research that supports national objectives by developing new technologies (e.g., carbon nanotube arrays, multiscale computational models, scanning probe nanolithography, and bioaerosol mass spectrometry) to combat chemical and bioterrorism, to monitor changes in the nation's nuclear stockpile, and to enable the development of advanced new methodologies for fundamental biology studies and human health applications.

- **Applied nuclear science for human health and national security**—nuclear science research that is being used to develop new methods and technologies for detecting nuclear materials, improving the treatment of advanced cancer, and assisting Laboratory programs that require nuclear and radiochemical expertise in carrying out their missions.

The directorate's organizational structure of divisions, centers, and institutes supports a team environment across disciplinary lines. This structure, which is summarized below, offers collaborative problem-solving opportunities that attract the best and the brightest from around the world.

- The **divisions** are responsible for the line management and the scientific, technical, and administrative leadership of the technical and administrative staff. Each division maintains a close relationship with Laboratory programs, working with directorate and program leaders to ensure an effective technical response to programmatic needs. The divisions conduct scientific and technical research in support of one or more of the four research themes.

- The **centers** provide specific research environments to support the nation's needs in biosecurity; chemical, nuclear, biological, and high-explosives counterterrorism; and research and development of explosives, pyrotechnics, and propellants.

- The programs at the **institutes** are tailored to reach a broad range of scientific talent, encourage and foster excellence, and attract quality scientists. Each institute provides a unique opportunity for outstanding students to experience "big science" in the dynamic environment of a national laboratory.

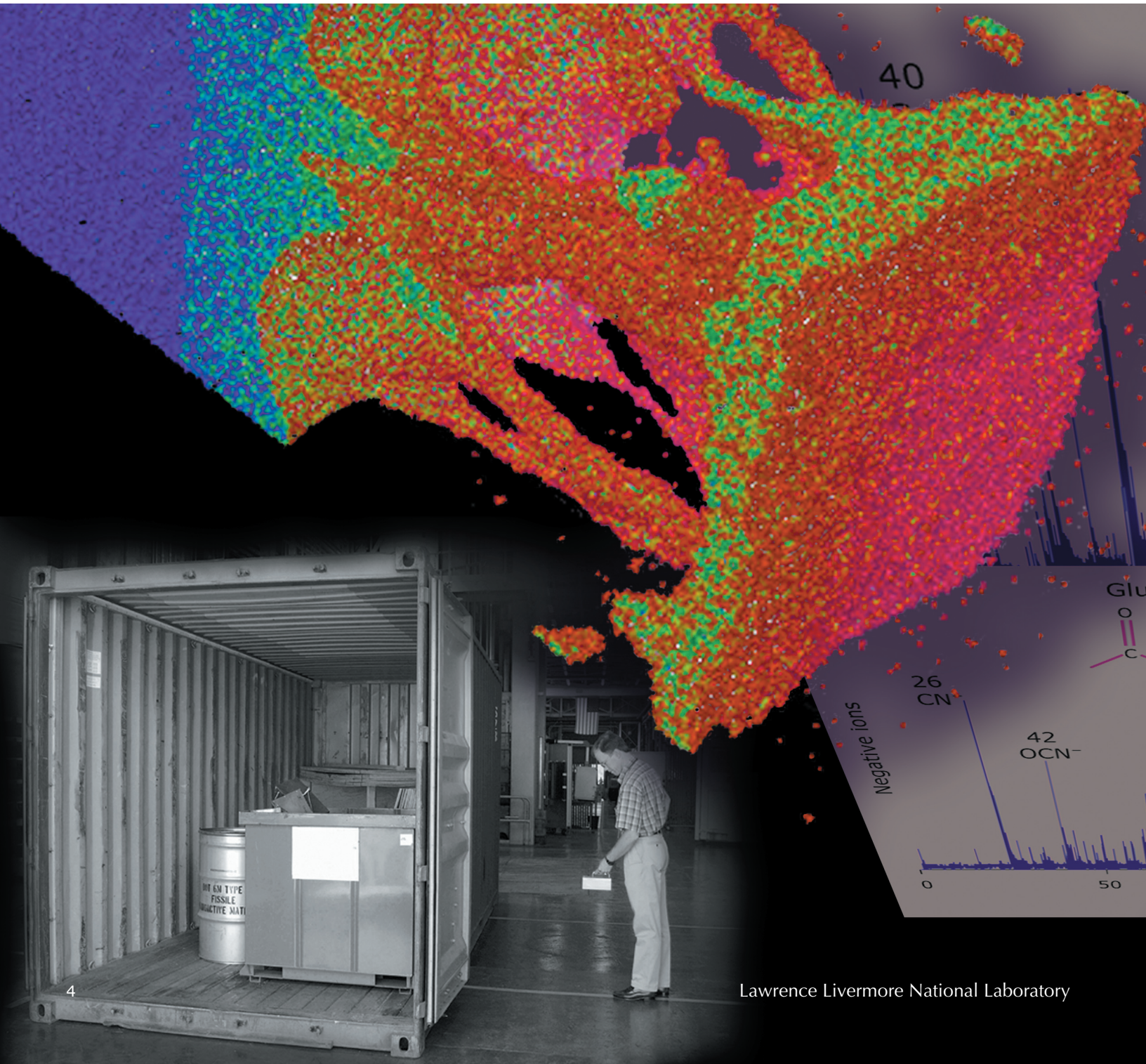
- The staff that makes the science happen continues to receive recognition for their accomplishments from their peers through awards, honors, and fellowships from respected scientific societies. See the **awards and recognition** section of this Annual Report, which highlights the many achievements in CMS during 2002.

This Annual Report provides an overview of our directorate and our efforts to support the Laboratory's national-security mission. This mission is even more crucial in the present day as we face an uncertain world and the new reality that the borders of our nation are not impenetrable. As Laboratory employees, we are reminded daily of the threat posed by terrorists and their arsenal of weapons and of our duty to serve our nation by ensuring its safety.

I am proud to be part of a team that faces these challenges with innovation and a sense of resolve. As we continue to strive toward excellence in the chemical and materials sciences, we eagerly anticipate the strengthening of our nation's safety and the advancement of the frontiers of science. We also look forward to continuing our legacy of partnership with the rest of the Laboratory as we achieve great things for our nation together.

Cheers,
Tomas

CMS Research Themes...



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Materials properties and performance...
Chemistry under extreme conditions...
Science in support of national objectives...
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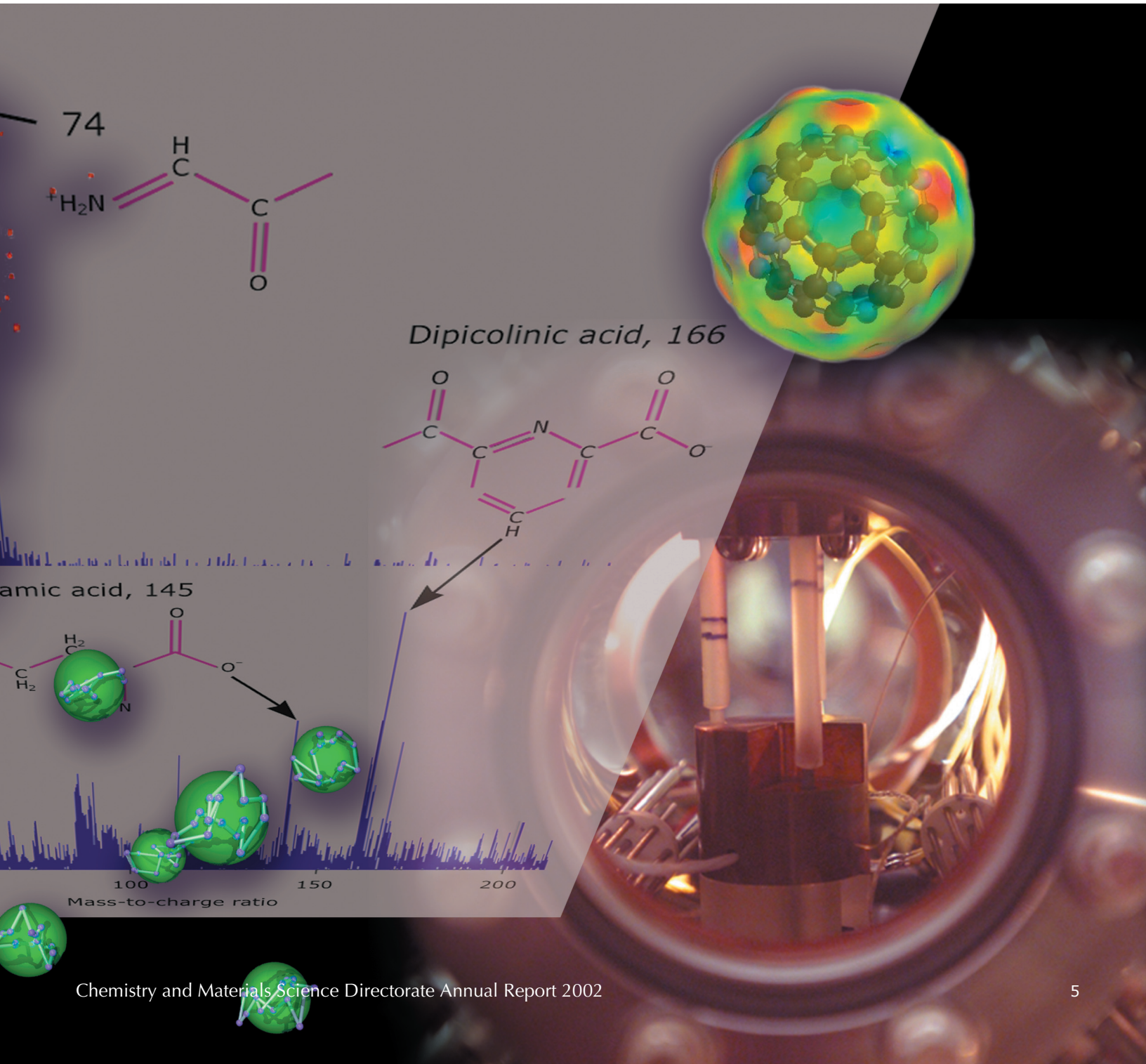

Dynamic Properties of Metals: Predictive Modeling

Predictions of materials response under extreme deformation conditions are needed to accurately assess the effects of aging on the performance of manufactured weapon parts. To meet this need, the materials dynamics research group at Lawrence Livermore is working to develop accurate models of materials response under extreme conditions.

This massive undertaking faces several challenges, including the lack of experiments that can directly measure materials strength under extreme deformation conditions and the inherently multiscale character of materials behavior under stress. Thus, to achieve our goal of predictive modeling, we have parsed the entire problem into computationally manageable length and time scales and are assembling these parts into an overall strength model.

The materials dynamics team members have a wide range of computational expertise, from electronic structure theory to solid mechanics and hydrodynamics. They include scientists from CMS and the Defense and Nuclear Technologies, Engineering, and Physics and Advanced Technologies directorates. The modeling tools that we have developed are being used to identify conditions in which the corresponding high-value experiments are most likely to validate our computer simulations.

Relevance to CMS Research Theme

Molecular dynamics (MD) research involves multiscale, multiphysics modeling of materials strength in extreme conditions. To create our models, we must first have a fundamental understanding of the atomistic mechanisms that underlie high-strain-rate deformation. We can then use this knowledge to develop computational capabilities that will provide accurate predictions of materials response.

Major Accomplishments in 2002

Unit Mechanisms of Crystal Plasticity

The plastic strength of a metal is defined by the behavior of its strain-producing defects, or dislocations. Consequently, dislocation mobility is the most basic ingredient of our computational hierarchy; if the mobility input is wrong, our final strength prediction will be inaccurate.

Because experimental observations of dislocation motion under high-stress and high-strain-rate conditions are almost impossible to obtain, direct atomistic simulations are used to investigate the mechanisms of dislocation motion in metals. We recently discovered that dislocations, contrary to prevailing views, can increase their mobility by tying one another into knots or junctions.

We also found that dislocation motion under stress can become rough and jerky, leaving debris in the form of lattice vacancies and interstitial clusters (Figure 1). This bizarre behavior is not caused by external factors, such as dislocation interactions with other crystal defects or impurities; instead, the roughening transition is intrinsic to the dislocation itself.

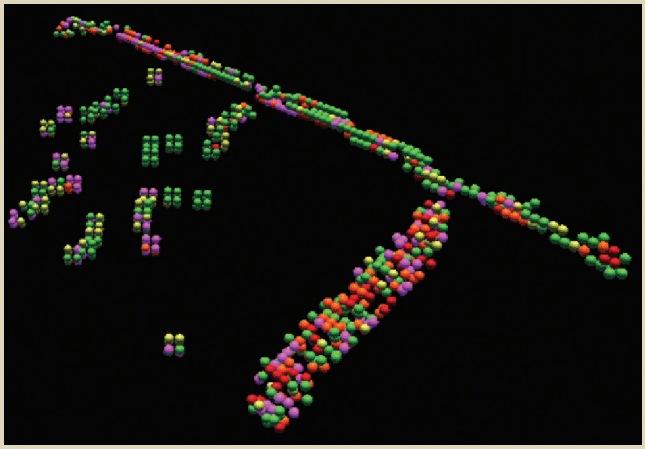

Figure 1. Self-pinning and roughening of screw dislocations in α-iron moving under high stress.

Realistic Simulations of Material Microstructure and Its Evolution under Stress

Assuming that dislocation dynamics models faithfully represent dislocation mobility, the remaining challenge is tracing the evolution of large populations of interacting dislocations over extended time intervals. Size matters in this situation because smaller models can neither capture collective effects nor span the length and time scales of dislocation microstructures that have been observed in experiments.

To achieve this relevancy, we are taking advantage of Livermore's massively parallel computing facilities. Our code, DD3D, recently produced simulations of up to 1 million dislocations, which were scalable on as many as 1024 processors. Using this new capability, we obtained the first clear modeling demonstration of naturally occurring strain hardening, which has been viewed as an ultimate challenge for dislocation dynamics methodology since the mid-1980s (Figure 2).

Future Goals

As we become more certain about the accuracy and reliability of our models, we must now modify our models so that they are suitable for simulating weapon part performance. This stage of materials dynamics research is very important because after more than 60 years of developing dislocation theory, we are finally able to effectively compute materials strength from the underlying physics of dislocation behavior.

New Frontiers

Microstructure and Shock-Induced Plasticity

We use ultralarge-scale atomistic simulations to examine how initial crystal defects (e.g., vacancies, interstitials, grain boundaries, dislocations, voids, and inclusions) affect the crystal's subsequent plasticity and strength under shocks. We have observed that after adding various defects to an otherwise pristine single crystal, the slope of the Hugoniot is barely affected, while the plasticity threshold reduces significantly.

Atomistic Modeling of Short-Pulse Laser Ablation

Laser ablation is being considered as a method for shaping the surface of targets at the National Ignition Facility. Laser machining can be used to rapidly form a wide variety of complex patterns. However, a serious limitation of the method is its tendency to leave a rough surface after ablation.

We have used MD simulations to investigate the causes of this roughening. Figure 3 shows an MD atomic configuration that was generated with a laser-energy pulse about 5 percent above the threshold for the significant removal of material. Although the surface remains smooth, the material below the surface is visibly roughened by the nucleation of large voids and the formation of liquid droplets and streamers on the two surfaces.

These types of surfaces are observed in experimental micrographs of copper after ablation, where the high thermal conductivity has rapidly frozen the ablated surface. These surfaces are also observed to a lesser extent in nickel, where the surface region remains molten for a longer time. The new knowledge provided by our simulations can be used to mitigate surface roughening for these materials.

Author

V. Bulatov

Related Publications

Bulatov, V. V.; Cai, W. Nodal Effects in Dislocation Mobility. *Physical Review Letters* **2002,** *89,* 115501.

Zbib, H. M. et al. A Multiscale Model of Plasticity Based on Discrete Dislocation Dynamics. *Transactions of the American Society of Mechanical Engineers* **2002,** *74,* 78.

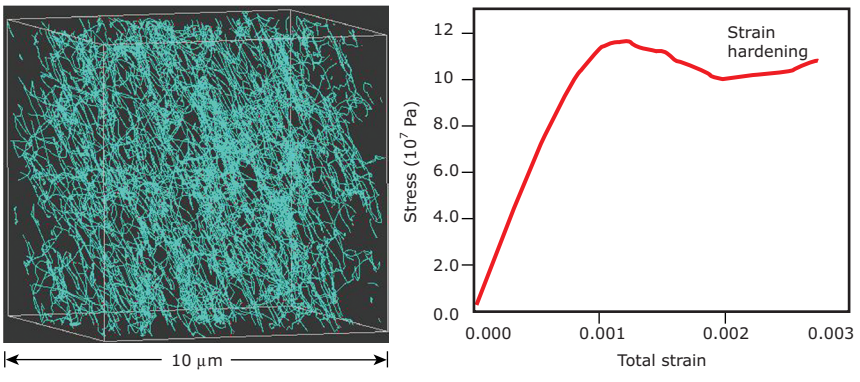

Figure 2. A dislocation microstructure developed in a dislocation dynamics simulation (left) that for the first time reproduced the strain-hardening behavior (right) observed in body-centered cubic single crystals under uniaxial loading.

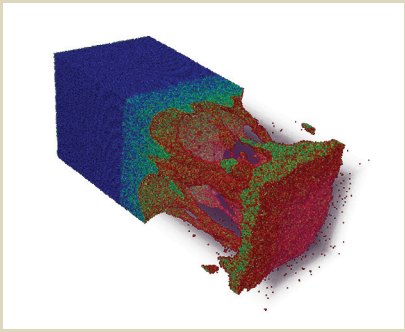

Figure 3. A molecular dynamics simulation of the ablation of copper using a 100-femtosecond, 800-nanometer laser pulse. Periodic boundary conditions were applied in the lateral directions only. The pulse energy of 0.2 joule per squared centimeter is about 5 percent above the ablation threshold.

Impulsive Stimulated Light Scattering in the Diamond Anvil Cell

To help us further understand the nature of the earth's magnetic field, tectonic motion, earthquakes, and volcanism, models of the underlying structure and chemical composition of the earth's interior have been developed. These models must now be linked with seismic data, a step that requires elasticity measurements under controlled conditions that imitate the conditions at the earth's core. These conditions include a pressure of more than 3.5 million atmospheres and a temperature of several thousand degrees at the center of the earth's core, which is primarily composed of iron.

Unfortunately, generating extreme, simultaneous conditions of pressure and temperature in a controlled fashion is difficult. The only device able to sustain the extreme pressure and temperature at the earth's core is the diamond anvil cell (DAC). However, the DAC has a major limitation, which is that it can only be used with very small samples (about one millionth of a gram or less). This stringent requirement effectively limits the use of otherwise appropriate methods, such as conventional ultrasonics and inelastic neutron scattering, to a small fraction of the DAC's potential pressure range.

Other methods for studying materials under extreme conditions also have limitations. For example, Brillouin scattering, which is the inelastic interaction of visible light with acoustic

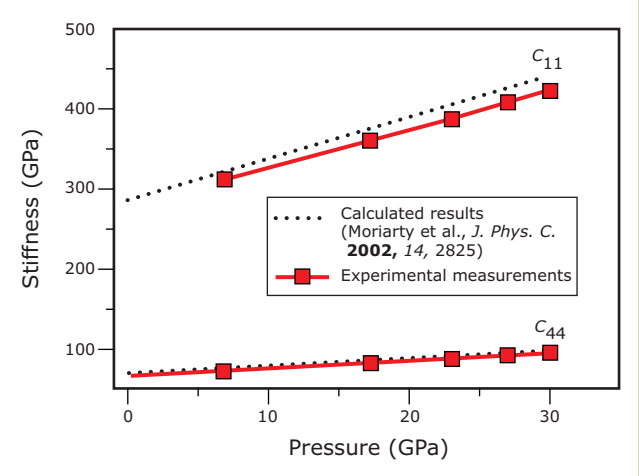

Figure 1. Two elastic stiffnesses (c_{11} and c_{44}) of polycrystalline tantalum that were obtained by combining the known bulk modulus of tantalum with acoustic wave velocities from impulsive stimulated light scattering measurements. Our experimental measurements (red) are within about 5 percent of theoretical calculations (black).

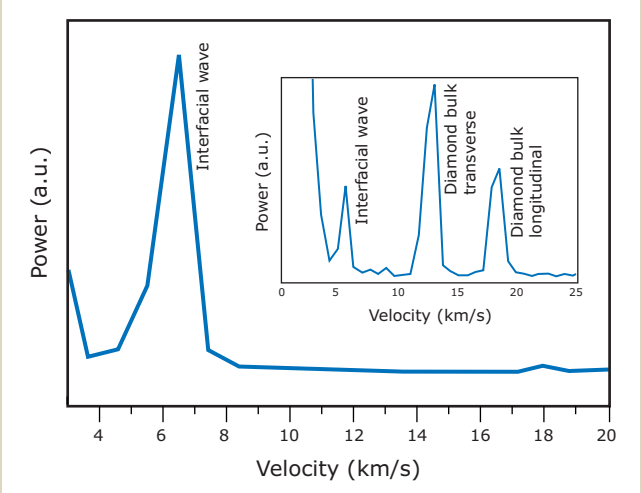

Figure 2. Impulsive stimulated light scattering spectrum obtained from the interface of diamond and iron at 23 gigapascals of pressure. Inset: The spectrum obtained at 13 gigapascals of pressure. Peaks due to the propagation of diamond bulk longitudinal and transverse waves are also present.

phonons, has been used to determine elastic properties at pressures up to 75 gigapascals. However, it is very difficult to apply Brillouin scattering to opaque materials such as metals.

Another method, inelastic x-ray scattering, shows great potential for studying metals, but it requires enormous x-ray fluxes to obtain sufficient experimental resolution, implying the need for a third-generation synchrotron. Furthermore, to obtain accurate values of the elastic stiffnesses from the x-ray data, assumptions regarding the shape of the phonon-dispersion curve must be made when extrapolating to zero frequency.

Relevance to CMS Research Theme

Impulsive stimulated light scattering (ISLS) is an ultrasonic technique that uses light to both generate acoustic waves and determine their velocity. Although ISLS has been used for several years in the DAC to study transparent materials, our group only recently demonstrated the applicability of ISLS to opaque materials, such as tantalum (Figure 1).

ISLS will enable us to make the elasticity measurements that are needed to link seismic data with structural and chemical-composition models of the earth's core. We can also use ISLS to examine the elastic properties of actinides (e.g., plutonium) and their analogs under extreme conditions—a subject of great programmatic importance.

ISLS measurements are extremely precise, with uncertainties of less than 0.5 percent under optimum conditions. In addition, ISLS experimental apparatus is modest in both size and cost.

Major Accomplishments in 2002

Construction of a state-of-the-art ISLS system in Building 235 was begun in February 2002 and was completed in June 2002. The system was used to make the first confirmed observations of a new type of acoustic wave in the surface-wave-power spectra of germanium single crystals.

We also measured iron's transition from a body-centered cubic structure (at about 11 gigapascals of pressure) to a hexagonal close-packed structure (at around 25 gigapascals of pressure) (Figure 2). These measurements represent a major achievement and suggest that ISLS can be used to study other structural transitions, such as that which occurs in plutonium at around 40 gigapascals of pressure.

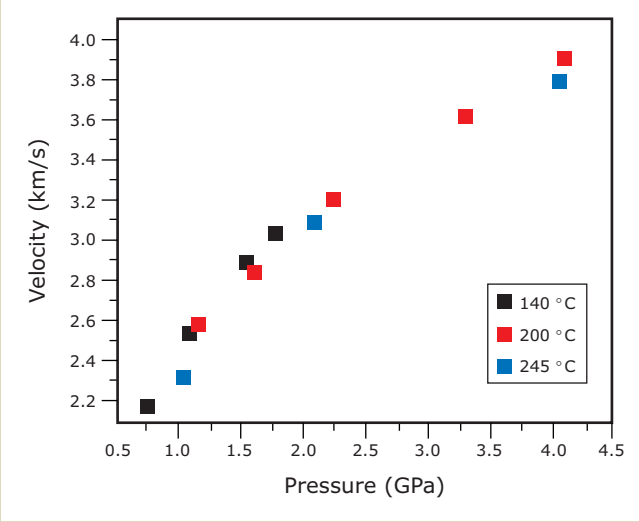

Figure 3. Speed-of-sound isotherms of formic acid that were obtained by using impulsive stimulated light scattering.

New Frontiers

The new ISLS system can be applied without modification to transparent materials, including solids, fluids, and fluid mixtures. High-pressure, speed-of-sound isotherms of liquid formic acid have already been obtained (Figure 3), and this data will be used to refine CMS scientist Larry Fried's thermochemical CHEETAH code.

Further measurements for this purpose will also be made on other transparent materials, such as formaldehyde, carbon dioxide, and mixtures containing carbon dioxide.

Future Goals

Given sufficient support from the Laboratory, we plan to extend our measurements of metal elasticity into the 100-gigapascal regime. We also intend to perform measurements under combined high-pressure, high-temperature conditions.

Authors

J. Crowhurst, J. Zaug, and A. Goncharov

Related Publications

Crowhurst, J. C. Surface Waves in Germanium Single Crystals. *Applied Physical Letters,* submitted for publication, 2003.

Crowhurst, J. C. et al. Surface Acoustic Waves in the Diamond Anvil Cell: An Application of Impulsive Stimulated Light Scattering. *Physical Review B* **2001,** *64,* 100103.

Nanomaterials Research: Nanoclusters, Quantum Dots, and Positrons

The range of CMS expertise in the growing field of nanomaterials continues to develop. The following sections examine current research in nanoclusters, quantum dots, and positrons.

Relevance to CMS Research Theme

The nanoworld is an extreme region affected by quantum-confinement effects and particle surfaces. The existing and potential uses of materials in this size regime are enormous. CMS nanomaterials research is an experimental demonstration of quantum-confinement theory. Our research helps answer basic questions about the structure–property relationship of low-dimensional materials. Our work also enables CMS to address nanoscience on the programmatic level.

Nanoclusters

Creating low-dimension materials in the nanometer range is of interest to materials scientists because nanomaterials exhibit new electronic, magnetic, and catalytic properties. In nanocluster physics, elementary building blocks (e.g., atoms and molecules) are used to fabricate materials with size-dependent properties. Because their properties can be tuned for use in different devices, nanoclusters show great promise as a new class of materials.

Major Accomplishments in 2002

Nanometer-sized diamonds (nanodiamonds) are found in systems ranging from interstellar dust to detonation residue. Nanodiamond K-edge absorption and emission spectra for 3- to 4-nanometer clusters showed the same features as the bulk material (diamond and graphite), and no blue shift was observed (Figure 1a), unlike in previous experiments. Calculations performed by J. Raty and G. Galli of the Physics and Advanced Technologies Directorate found that the surfaces of particles larger than 1 nanometer reconstruct in a fullerene-like manner, giving rise to fullerene-capped diamond clusters (Figure 1b). Pre-edge features in measured spectra were consistent with these surface reconstructions.

Quantum confinement is responsible for changes in the band gap of nanometer-sized semiconductor

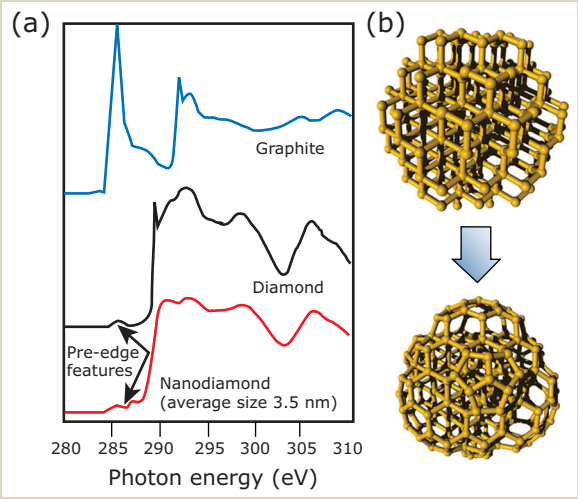

Figure 1. (a) Carbon K-edge x-ray absorption spectra for graphite, diamond, and nanodiamond. (b) Ball-and-stick representation of ideal (top) and surface-reconstructed (bottom) nanodiamonds. The difference in the pre-edge features for diamond and nanodiamond in (a) indicates fullerene-like surface reconstruction on the nanodiamond, which has been confirmed by computer simulations by Raty and Galli in (b).

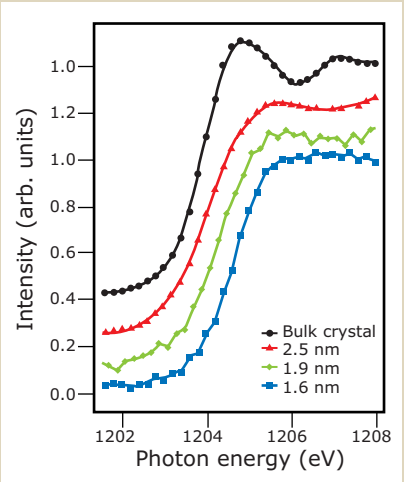

Figure 2. Germanium L-edge absorption spectra for a bulk crystal and three nanocrystal samples. The absorption edge moves to higher energies with reduced particle size.

materials (Figure 2). We developed a gas-phase-based synthesis route to produce nanocrystals with a narrow size distribution. In our experiments, clean germanium nanocrystal films exhibited stronger quantum-confinement effects at the band edges than did similar silicon particle films.

To investigate surface-passivation effects on the electronic structure of nanocrystals, we developed a method for the in situ termination of bare particles. In thick films of passivated nanocrystals, the passivating agent altered the electronic structure of the assembly. The absorption edge shifted to higher energies than in cluster films without surface passivation.

Future Goals

Future experiments will examine the stability of diamond and germanium at the nanoscale. We will use our in situ passivation technique to examine the impact of surface modification on the nanocrystal electronic structure—and thus, optical properties—of more complex nanomaterials.

Quantum Dots and Positrons

Reliable nanostructure production is needed for many applications (e.g., semiconductor electronics, optical devices, quantum communications, and quantum computing). Because the quality and integrity of the quantum dot and its environment play key roles in the success of a device's function and in its applicability, understanding the electronic properties of quantum dots is essential. Our research uses positron annihilation spectroscopy to investigate these properties. In this technique, the Doppler broadened momentum annihilation line shape results from the momentum of the electron with which the positron annihilated and can be used to probe the electronic structure and electron momentum distribution.

Major Accomplishments in 2002

Positron annihilation was observed in 1.8- to 3.6-nanometer CdSe quantum dots and was compared with positron annihilation in bulk CdSe. This work was performed in conjunction with Washington State University; Northeastern University; and Technical University, Delft, the Netherlands. Most positrons produced in a low-energy beam were trapped inside CdSe and annihilated with valence electrons in CdSe. Quantum-mechanical calculations using the Korringa, Kohn, and Rostoker (KKR) method were compared with CdSe quantum dot data. The calculations showed a reduction of the Cd (4d) electron contribution for the dots relative to the bulk crystal. This effect has tentatively been ascribed to a reduction in positron annihilation at the cadmium surface sites due to the complete binding of the surfactant to cadmium, leaving selenium available for electron annihilation (Figure 3).

Future Goals

We plan to use the new spectrometer at Livermore's Intense Positron Beam Facility to make Doppler spectroscopy measurements. We will continue to investigate the electronic structure of quantum dots as a function of size and will develop a diagnostic tool to interrogate their quality and integrity. We will also examine metallic quantum dots.

Authors

T. van Buuren and C. Bostedt (Nanoclusters); A. Denison (Quantum Dots and Positrons)

New Frontiers

Electronic systems of nanoparticles can improve the ability to communicate quickly and accurately by handling large amounts of information, including computational tasks. These systems can also detect small signals in a variety of applications and environments. Work is underway to use nanoparticles to develop detectors for nuclear, toxic, or pathogenic materials in the atmosphere or in other environments.

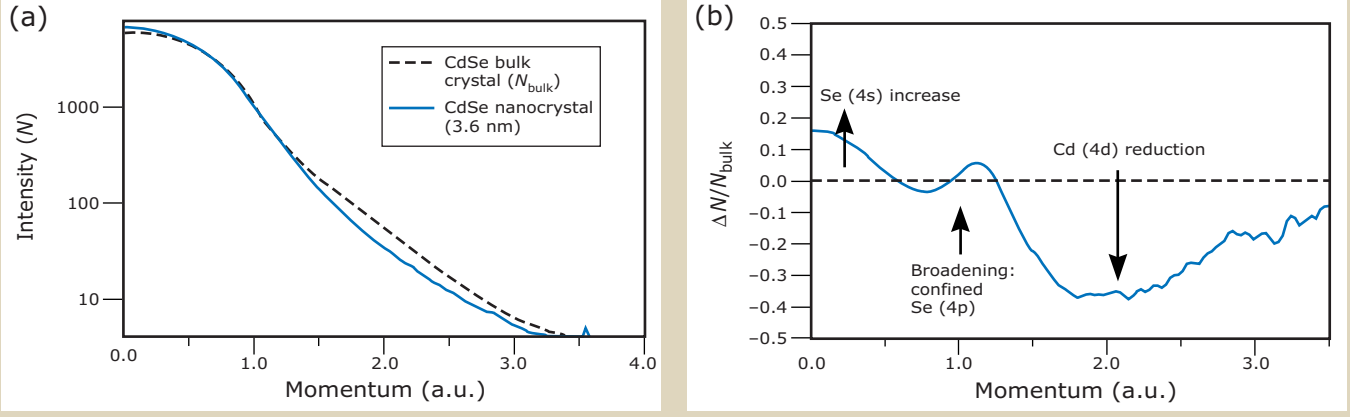

Figure 3. (a) A comparison of Doppler broadening of CdSe quantum dots with bulk CdSe. (b) The ratio of the signals in (a), showing the changes caused by preferential annihilation of positrons at selenium-terminated surfaces. (These calculations were contributed by our collaborators at Technical University, Delft, the Netherlands.)

Recent Advances in Plutonium Science

At ambient pressure, plutonium exists in six allotropic forms (the α-phase, which is the ground-state structure and is stable at temperatures below 100 °C and the β-, γ-, δ-, δ′-, and ε-phases). Each phase exhibits a unique crystal structure and peculiar physical and chemical properties.

Plutonium phases—some of which are still uncertain or unknown—may also emerge at high pressures, as generated in diamond anvil cells or during shock deformation. Adding gallium to plutonium may eliminate the β- and γ-phases and allow retention of the δ-phase. However, even when retained, plutonium behavior is complicated by the interplay between its electronic structure and its physical properties.

Because plutonium is so complex, materials scientists believe that knowledge about plutonium behavior, once acquired, will enable them to easily explain the behavior of other elements. This, in essence, is the lure and challenge of plutonium science.

Relevance to CMS Research Theme

Accurate simulations and models of plutonium behavior are needed to forecast how aging plutonium may affect the U.S. nuclear stockpile. However, any attempts to predict the behavior of aging plutonium must take into account the complex nature of plutonium, as well as the effects of radiation as plutonium decays into uranium and helium.

Scientists and engineers in the Materials Science and Technology Division are intimately involved in the surveillance of crucial materials and components in the present stockpile. They are examining the changes in materials properties at the atomic, microstructural, and macroscopic levels; constructing physical models for the evolution of these changes; and then predicting how these changes will affect performance under extreme conditions of high-speed deformations, pressure, and temperature.

Major Accomplishments in 2002

We used our 300-kiloelectronvolt, state-of-the-art, analytical transmission electron microscope (TEM) to examine plutonium specimens. Special procedures for TEM sample

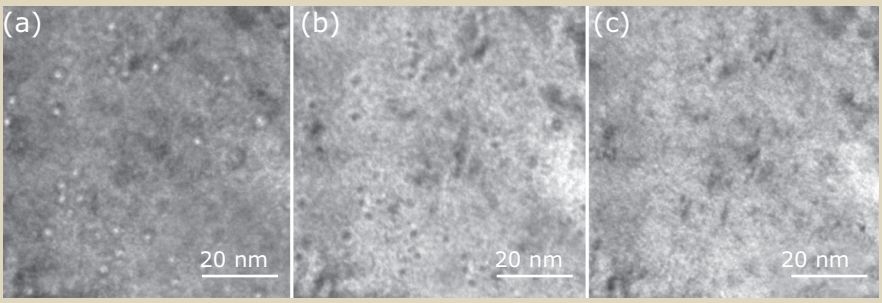

Figure 1. Transmission electron microscopy images of a 42-year-old plutonium alloy. The images were obtained by using the through-focusing technique to identify atomic-sized helium bubbles. (a) The underfocused image (–1.4 micrometers) shows the high density of very small helium bubbles as a dark fringe surrounding a light dot. (b) In the overfocused image (+1.4 micrometers), the bubbles appear as light fringes surrounding a dark dot. (c) The bubbles do not appear in the in-focus image.

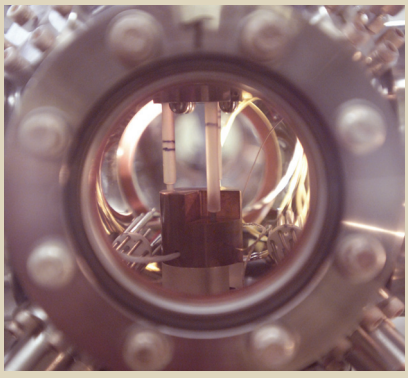

Figure 2. The experimental setup for measuring the lengths of enriched plutonium specimens (contained in the reddish-brown copper block). Measuring rods are placed on top of the samples.

preparation enabled us to detect, for the first time, the nanometer-sized helium bubbles that form in plutonium as it ages (Figure 1). By combining TEM measurements of the bubbles with theoretical modeling and measurements of positron annihilation lifetimes, we determined the helium density in the bubbles to be extremely high—the equivalent of three helium atoms for each missing plutonium atom.

One potential plutonium-aging mechanism is the radiation-induced formation of voids, or cavities. By combining molecular dynamics computer simulations of voids with theoretical models of void collapse, we discovered that extremely high pressures are needed to collapse voids measuring a few nanometers in diameter. This critical collapse pressure decreased as void diameter increased. Using this information, we developed and validated an equation of state for metals with voids and helium bubbles.

From studying the resistive properties of radiation damage in δ-phase plutonium–gallium alloys, we learned when and how vacancies and interstitials move and annihilate with temperature. The resistance of the vacancies exhibited an exponential inverse temperature dependence indicative of a complex electronic structure. Our resistive method was also used to detect the change in plutonium from δ- to α-phase as a function of temperature and to monitor δ-stabilized plutonium–gallium alloys in the nuclear stockpile.

Future Goals

Adding plutonium-238 to plutonium–gallium alloys increases the rate of radioactive decay. CMS metallurgists have enriched material otherwise identical to stockpile material with 7.5 percent plutonium-238. This enrichment level accelerates aging by a factor of 16. Rod specimens of the enriched material are being monitored for length changes and will continue to be monitored for the next five years.

Figure 2 shows the experimental setup that keeps specimen pairs at preset aging temperatures, measures and collects any temperature fluctuations, and continuously records specimen length. The use of specimen pairs that are identical except in initial length enables us to subtract any length changes resulting from oxidation.

New Frontiers

The question of how gallium stabilizes the δ-phase of plutonium has intrigued physicists and metallurgists since the Manhattan Project. A recent investigation of this problem combined density functional theory and spin- and orbital-polarization to perform calculations on α-plutonium.

The first calculations were performed in periodic supercells containing 16 and 32 atoms. All atom positions, as well as the lattice parameters of the unit cell, were fully relaxed. Figure 3 compares the calculated and experimental atomic volumes of plutonium in each lattice site of the α-crystal structure. These volumes are defined by Voronoi cells constructed around each atom.

The experimental volumes represent the x-ray diffraction results at room temperature, reduced by 5 percent to account for the thermal expansion contribution. The first-principle molar volumes are 5 percent smaller than extrapolations of the measured volumes, but this discrepancy is typical of density-functional-theory calculations. It is remarkable that theory reproduces the different atomic volumes of plutonium found in the α-structure.

Authors

A. Schwartz, W. Wolfer, and M. Fluss

Related Publications

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Nelson, E. J. et al. Local Structure and Vibrational Properties of α′-Pu Martensite in Ga-Stabilized δ-Pu. *Physical Review B,* submitted for publication, 2003.

Schwartz, A. J. et al. Characterization and Modeling of Helium Bubbles in Self-Irradiated Plutonium Alloys. *Philosophical Magazine,* submitted for publication, 2003.

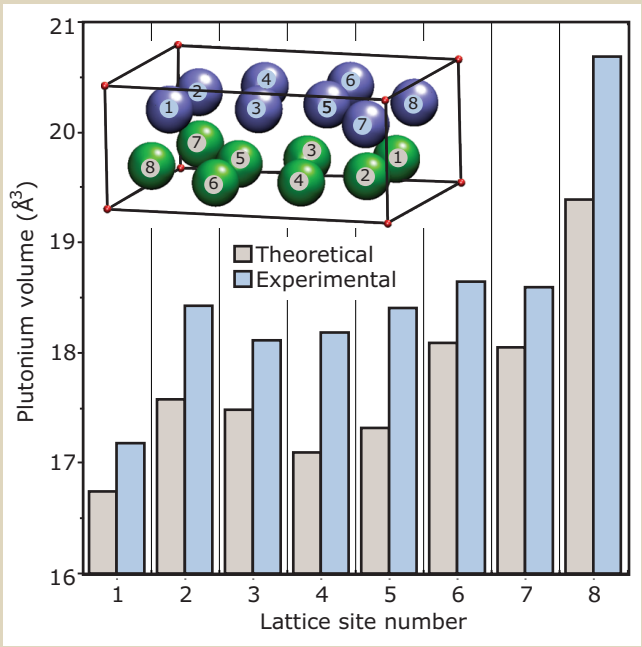

Figure 3. A comparison of the experimental and theoretical atomic volumes occupied by plutonium in each lattice site of the α structure (see inset). On average, the theoretical atomic volumes are 4.3 percent lower than the values obtained from x-ray diffraction data.

Strain-Rate Scaling of Deformation Mechanisms

Materials science at ultrahigh pressures and strain rates is an emerging field. Over the past six years, research at high-energy-density facilities, such as the Nova and Omega lasers, has shown that with careful control of the drive-pulse shape, solid-state samples can be compressed under extreme states of pressure and strain rate without changing phase.

Relevance to CMS Research Theme

Our research examines the mechanisms (e.g., slip or twin) by which solid-state samples deform, the sensitivity of these mechanisms to shock, and the changes in these mechanisms at different levels of pressure and strain rate. Determining these underlying mechanisms of materials deformation is critical for establishing constitutive models that can be used to simulate material response to high pressure.

For example, the magnitude of a material's flow stress (i.e., material strength) and its functional form depend on the material's specific deformation mechanism. However, deformation mechanisms, such as shear localization (banding) and nucleation-controlled phase transformations, can be affected by a change in length scales, as in the case of short-pulse-loading profiles. Consequently, investigating both deformation mechanisms and their scalability will show whether mechanisms that are discovered at ultrahigh pressures and strain rates can also be applied to regimes at lower strain rates.

Our group is addressing these issues by demonstrating the viability of laser-driven experiments, when coupled with recovery and characterization, in mapping deformation mechanisms across a wide range of pressures and strain rates. We are also examining the scalability issue by conducting simulations based on continuum codes and molecular dynamics (MD), as well as by performing experiments at multiple facilities: the Omega and National Ignition Facility (NIF) lasers, Livermore's gas gun, and the Sarov high-explosive facility.

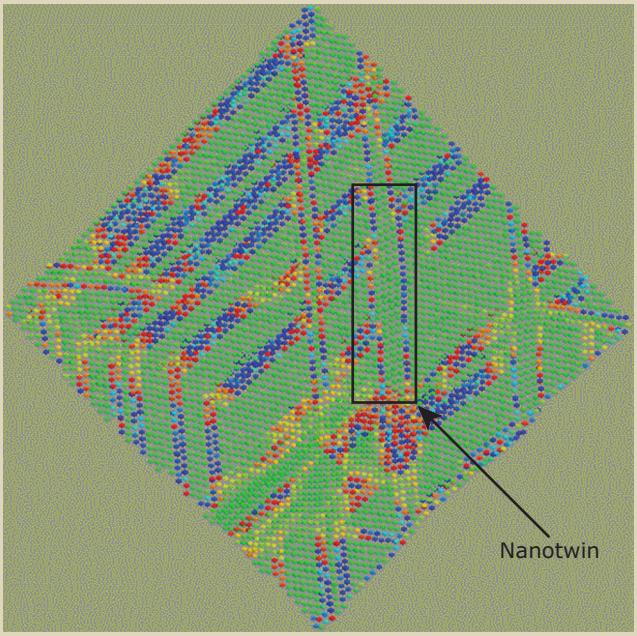

Figure 1. A molecular dynamics simulation showing twin formation in single-crystal copper at 10.81 picoseconds after applying a 50-gigapascal shock.

Major Accomplishments in 2002

We have developed an experimental platform for our shockless laser-driven experiments that uses copper as a model material. Both single-crystal and polycrystalline samples have been loaded to pressures ranging from 10 to 50 gigapascals. We are currently analyzing recovered samples from these experiments, and we expect the results of these analyses to accurately characterize the transition from the slip deformation mechanism to the twin deformation mechanism.

Our MD calculations have shown a twinning transition in single-crystal copper under shock-loading conditions at a pressure of 50 gigapascals (Figure 1). In addition, our work is being used to develop recovery techniques and characterization methodologies for materials-science-based experiments at NIF.

Future Goals

One experimental goal is to use the laser-based shockless drive to finish the slip/twin deformation map for laser-driven polycrystalline and <100> copper at high pressures and strain rates. We will also examine single-crystal orientation and grain-size effects. In addition, we will investigate scalability through the use of shockless drives in both high-explosive and gas-gun facilities.

We will also develop shockless loading techniques for MD-based calculations. Our new simulations will examine the deformation structures produced during shock loading and will assess their subsequent stability. Future calculations will investigate the effect of grain boundaries and defects (impurities, vacancies, and interstitials) on the slip/twin transition. Finally, we plan to use crystal plasticity-based calculations to address the formation of shear bands under the vastly different time scales present in laser-driven experiments versus those generated by high-explosive or gas-gun drives.

Authors

B. Remington and J. McNaney

Related Publications

Edwards, J. et al. A Laser-Driven Plasma Loader for Shockless Compression and Acceleration of Samples in the Solid State. *Physical Review Letters,* submitted for publication, 2003.

McNaney, J. M. et al. High-Pressure, Laser-Driven Deformation of an Aluminum Alloy. *Metallurgical Transactions A,* submitted for publication, 2003.

New Frontiers

Laser-Driven Shock Compression of Matter

Direct irradiation of solid material with a 1-micrometer-wavelength laser beam, can generate approximately 100-kilobar shocks, with a beam intensity of about 10^{11} watts per square centimeter. This experimental setup enables the study of materials-dynamics behavior under shock loading with a few tens of joules from a tabletop laser in a spot size of a few millimeters and a pulse duration of a few nanoseconds.

However, by confining ablations, we can generate the same 100-kilobar pressures with less laser intensity—about 10^{9} watts per square centimeter. The lower intensity means that longer pulses and wider spots can be used with the same pulse energy. Longer pulses maintain shock pressure for a greater amount of time so that the higher pressure reaches a greater sample depth. Such pulses are useful in materials-dynamics studies and materials-processing applications that must propagate higher-pressure pulses over several grain lengths in the material.

Confining ablation pressure can be achieved by sending a laser beam through a transparent dielectric, or tamper, that is in contact with the ablation layer and material sample. The threshold for dielectric breakdown of typical tamper materials is greater than 10^{10} watts per square centimeter, although there may be a lower threshold for damage caused by surface defects.

Studies of material behavior under shock loading and studies of material fracture and failure require details about the pressure morphology throughout the material (e.g., how it relates to the precise temporal shape of the laser pulse). To provide these details, a computational model must include prescriptions for all relevant physical processes over the wide range of temperatures, densities, and absorptivity levels found in solid metals and ablated plasmas.

Scientists in the Materials Science and Technology Division, in collaboration with scientists in other directorates, have developed such a model for low-intensity laser drives and have incorporated the model into the LASNEX code. The model includes prescriptions for calculating

- the correct ionization state and electron densities for metals from a Drude model;
- the electron densities for insulators as a function of temperature from the band theory of solids;
- the low-intensity absorption of a laser beam on a solid or liquid metal;
- the photoionization absorption of a low-intensity laser beam in neutral vapor;
- the collisional ionization, three-body recombination, and dielectric breakdown.

The new computational model has been benchmarked against experimental data and is being refined and applied to problems of interest to the Laboratory. For example, the model has been applied to the study of spall and material damage in tin as part of the Laser-Shock Diagnostics Project in the Enhanced Surveillance Program.

CMS Contact: J. Colvin

Related Publication

Colvin, J. D. et al. Computational Model for a Low-Temperature Laser–Plasma Driver for Shock Processing of Metals and Comparison to Experimental Data. *Physics of Plasmas,* in press.

Advanced Sol-Gel Synthesis

It is well known that mechanical, acoustic, electronic, and optical properties can be significantly and favorably altered in nanostructured composite materials. Energetic nanocomposites are a class of materials that have fuel and oxidizer components intimately mixed and where at least one component has particles that are less than 100 nanometers in dimension. One example of an energetic nanocomposite is the sol-gel-derived pyrotechnic, in which metal–oxide nanoparticles react with nanometer-sized fuel metals in exothermic reactions (Figure 1).

Because the initiation and detonation properties of these energetic materials are dramatically affected by their microstructural properties, sol-gel chemistry can be used to manipulate desired properties. In addition, by enabling the control of structures at the nanometer scale, sol-gel chemistry provides a way to form new energetic materials with improved, exceptional, or entirely new properties.

Our goal is to advance the preparation of tailored materials with "designer" properties. However, to more effectively engineer porous materials with desired features (e.g., mechanical strength and porosity), we must first understand the kinetics and thermodynamics of sol growth. Thus, the current focus of our research is on determining the influence of synthetic and processing conditions on the microstructure of porous, low-density, open-cell foams. Advancements in this area could lead to a broad range of applications including catalysis, separation technology, ceramics, sensors, detectors, and nanoelectronics.

Relevance to CMS Research Theme

The constant discovery and development of advanced materials are integral parts of the advancement of science and technology at the Laboratory. CMS supports this endeavor through the investigation of chemistry and materials under extreme conditions. The synthetic methods developed at Livermore (e.g., the epoxide addition method) allow us to examine new or alternative synthetic routes to meet criteria such as composition, purity, physical properties, and yield for advanced materials.

Applying sol-gel chemistry to the synthesis and processing of advanced materials is part of a broader effort that includes preparing and evaluating very low-density metal and metal–oxide foams, stronger and tougher nanoceramics, and energetic nanocomposites, as well as contributing to the fundamental science and technology of sol-gel chemistry.

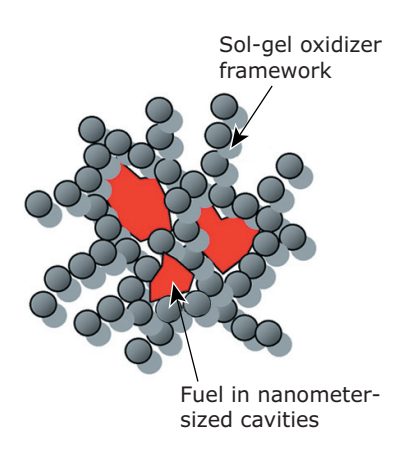

Figure 1. A sol-gel-derived energetic nanocomposite. The sol-gel framework consists of an interconnected nanometer-sized oxidizer, and the fuel component resides in the nanometer-sized cavities of the oxidizer's framework.

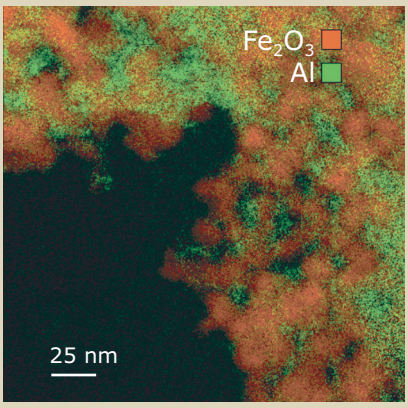

Figure 2. An energy-filtered transmission electron microscopy of a sol-gel-derived Fe_2O_3/Al nanocomposite illustrates the extremely fine mixing of oxidizer and fuel achieved via the sol-gel process.

The sol-gel approach for energetic-material processing offers the possibility of precisely controlling oxidizer–fuel compositions and producing composites with extremely well-dispersed and intimately mixed component phases. By minimizing the particle size of oxidizers and fuels (Figure 2), we can increase the power of high-energy-density composites. Our sol-gel energetics efforts also provide expertise for the synthesis and formulation of new reactive fragments that are stable at high temperatures.

Major Accomplishments in 2002

We have improved the mechanical properties of iron(III) oxide aerogels (Figures 3a and 3b) so that β-FeOOH aerogel materials can be machined into parts with desired dimensions. This led to the preparation and use of β-FeOOH aerogel parts as precision targets in high-energy-density physics experiments. A by-product of this work led to the first monolithic Fe_2O_3 magnetic aerogel (Figure 3c).

There has also been a recent development in the application of energetic nanocomposites as precise, stable, and nontoxic igniters for small- and medium-caliber munitions. CMS team collaborations have produced impact-sensitive devices that are strong candidates to replace the hazardous powders currently used in primers and stab detonators.

We have also applied new sol-gel methods that were developed at the Laboratory to efficiently synthesize nanometric ceramics. These ceramics exhibit a fracture toughness that is significantly higher than that of the ceramics produced through current synthetic methodologies.

Future Goals

We plan to characterize the sol-gel polymerization process on the molecular scale so that solution processes can be correlated with the final microstructures and properties of advanced materials. We are also pursuing attempts to process sol-gel energetics into composite parts that can withstand extreme launch conditions.

Authors

A. Gash, T. Baumann, and J. Satcher, Jr.

Related Publications

Gash, A. E. et al. New Sol-Gel Synthetic Route to Transition and Main-Group Metal Oxide Aerogels Using Inorganic Salt Precursors. *Journal of Non-Crystalline Solids* **2001,** *285,* 22.

Gash, A. E. et al. Use of Epoxides in the Sol-Gel Synthesis of Porous Iron(III) Oxide Monoliths from Fe(III) Salts. *Chemistry of Materials* **2001,** *13,* 999.

Tillotson, T. M. et al. Nanostructured Energetic Materials Using Sol-Gel Methodologies. *Journal of Non-Crystalline Solids* **2001,** *285,* 338.

New Frontiers

University Research

Although the potential benefits of energetic nanomaterials applications are well-known, the fundamental science behind the combustion and energy-release mechanisms of energetic nanocomposites is not yet fully understood. We are collaborating with several universities to study these mechanisms so that we can eventually reap the full potential of energetic-nanomaterials applications. Current university collaborations include the following:

- Dr. Michelle Pantoya at Texas Tech University is evaluating the ignition, energy release, and burn characteristics of energetic nanocomposites.
- Drs. Michael Zachariah and Alon McCormick at the University of Minnesota are synthesizing energetic nanomaterials.
- Dr. Thomas Brill at the University of Delaware is examining the safety properties of sol-gel energetics.

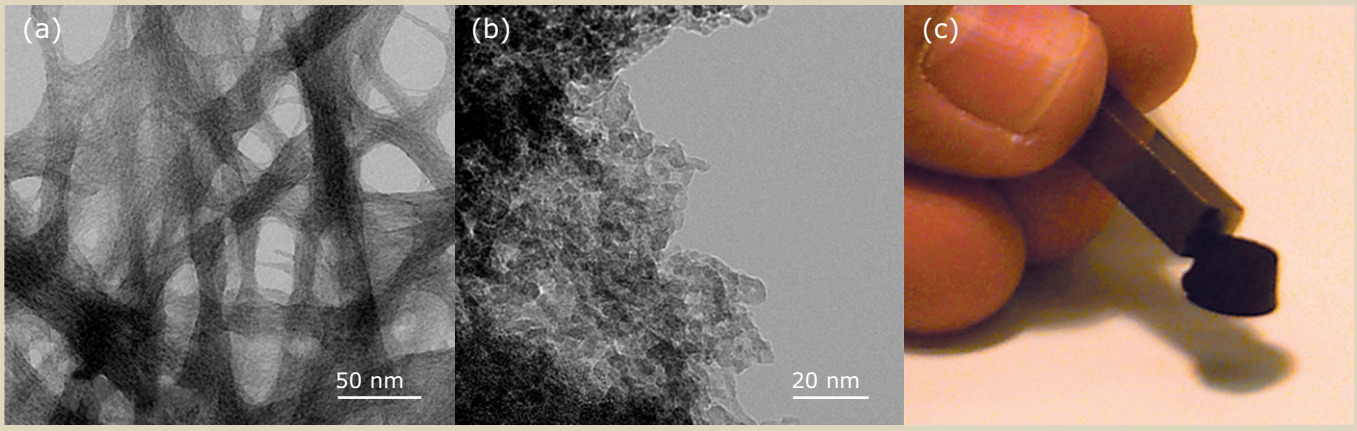

Figure 3. Transmission electron micrographs of iron(III) oxide aerogels made with (a) 3,3-dimethyl-oxetane and (b) propylene oxide. The aerogel in (a) has markedly better mechanical properties than the one in (b). (c) Photo of a magnetic iron(III) oxide aerogel. Characterization revealed that the iron(III) oxide is maghemite (magnetic Fe_2O_3).

Quantum Molecular Vibrations: A New Frontier in Computational Chemistry

A highly accurate fundamental understanding of molecular structures and properties of all but the smallest of molecules has eluded scientists. Once known, this information will have implications for defense applications (the thermodynamics of detonation products), atmospheric science, and fundamental science.

The vibration of a molecule is a quantum-mechanical phenomenon. Current treatment of molecular vibrations in quantum chemistry is usually based on harmonic oscillator approximations. However, wide classes of molecules (e.g., those in which proton transfer is significant and those in which torsional angles are present) do not behave as simple harmonic oscillators because the interplay between electronic effects and anharmonic quantum vibrations can be very strong. Traditional approaches ignore these effects, thereby missing crucial physics (e.g., overestimating heat capacity).

Relevance to CMS Research Theme

Our group is defining a new scientific area: simultaneously fully quantum mechanical treatment of both nuclei and electrons. This allows us to study molecules under extreme conditions (high temperatures and metastable chemical species).

We have developed a path-integral Monte Carlo (PIMC) code to explore quantum effects in chemical systems. This fully quantum picture will provide insights into the chemical reactions of energetic materials that are directly relevant to the Laboratory's stockpile stewardship mission. In addition, our work on chemical systems, such as carbine (CH_2^+), carbene (CH_2), water (Figure 1), and nitrogen hydride (NH_2), is useful in calculating chemical kinetic rates, which will give us needed knowledge about conventional explosives.

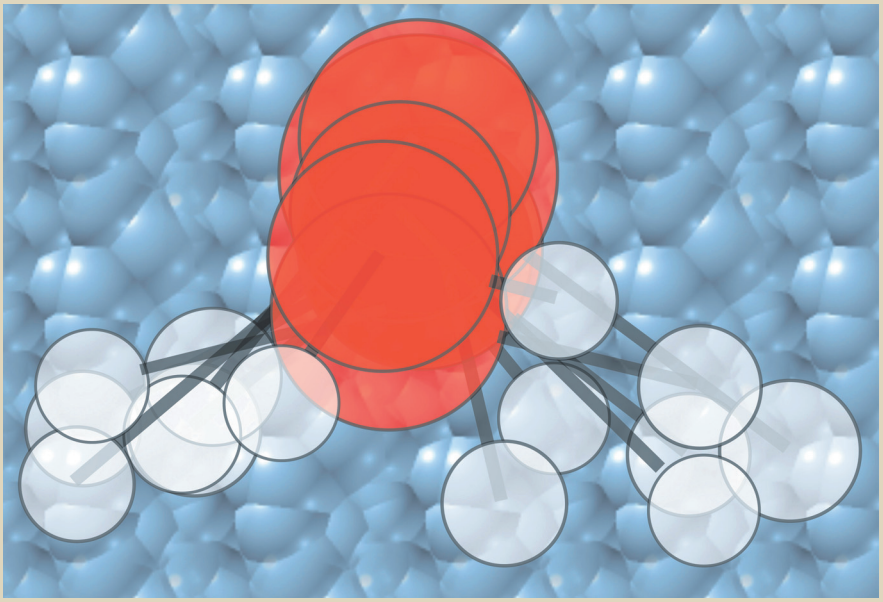

Figure 1. A single water molecule (H_2O) is quantum-delocalized with path integrals.

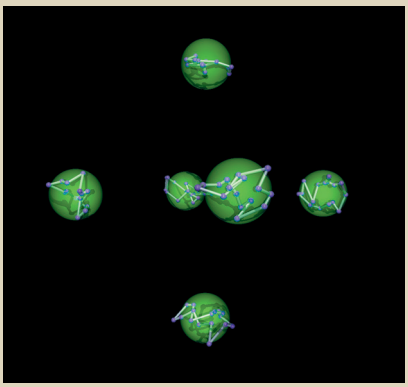

Figure 2. An Ar_6 cluster under the extreme conditions of 1 kelvin. Within the path-integral Monte Carlo methodology, each classical atom (large green balls) is delocalized into a path of 16 replicas (small purple balls).

Major Accomplishments in 2002

Our research scope combines a quantum treatment of electrons via ab initio methods with a quantum treatment of nuclei via PIMC. We have developed theoretical techniques and computational methods that make calculating accurate chemical properties feasible. Our research is the first to use a high-level treatment of electron correlation through methods such as Møller–Plesset perturbation theory, enabling us to study proton transfer and other problems involving long-range electron correlation.

Our project initially focused on generating an efficient, massively parallel PIMC code. This code, which is being used to explore quantum effects in chemical systems, allows us to study fundamental scientific questions about structure and bonding. A novel data-caching scheme has also been implemented to significantly speed up Monte Carlo sampling.

Future Goals

The PIMC code and theoretical methods developed in our research will be applied to additional chemical systems to gain thermochemical knowledge. By calculating the thermodynamic properties of molecules on the computer instead of in the laboratory, molecules with short lifetimes (Figure 2) can be studied as easily as more traditional molecules. We can then calculate properties for the Joint Army, Navy, and Air Force thermochemical reference tables. This data can be used by thermodynamic modeling codes, such as CHEETAH, to calculate material properties.

We will also apply the PIMC method to larger chemical systems. In this area, we are benefiting from collaborations with scientists, such as Dr. J. Lewis at Brigham Young University, on problems such as proton positioning within molecules.

New Frontiers

Aromaticity Provides Bucky Stability in Aza-Fullerenes

Attempts to replace carbon atoms in the C_{60} fullerene molecule with nitrogen atoms have produced opportunities to fine-tune the structural, electronic, and conductive properties of C_{60}. A recently synthesized, nitrogen-substituted fullerene material was shown to have the $C_{48}N_{12}$ molecule at its core. The molecule's proposed structure contained one nitrogen atom in each pentagon, which would stabilize the molecule by minimizing repulsive nitrogen–nitrogen interactions.

However, through a series of quantum-mechanical, density-functional calculations, our research group has demonstrated an even more stable structure of $C_{48}N_{12}$ (Figure 3). Our calculations showed that the stabilizing role is played by the extended aromaticity of the eight all-carbon hexagonal rings. In our proposed structure, there is one nitrogen atom per pentagon, and a triphenylene-type unit is connected to three nitrogen atoms at both the top and bottom of the aza-fullerene. The 18 electrons in each unit are distributed to give the outer rings a benzene-like sextet, while the six remaining nitrogen atoms lie around the fullerene's equator. The extended region of electron delocalization provided by these two units enhances the molecule stability through resonance energy, while precluding a weaker nitrogen–nitrogen link. The resulting structure is 0.5 electronvolts more stable than the previously reported structure.

Our research group has also studied new nitrogen–nitrogen-linked, fullerene-analog structures of $C_{48}N_{12}$ with six N_2, four N_3, and two N_6 subunits. Such structures can be considered to be high-energy-density forms, with relative energies of 4.5, 8.2, and 11.4 electronvolts. Figure 4 shows the structure with two N_6 rings. This extended carbon composition could stabilize pyrazole, triazole, or even benzene-like rings of nitrogen—a leap toward the realization of high-symmetry structures of polynitrogen. Further work on the boron–carbon analogs of these structures is in progress.

CMS Contact: M. Manaa

Related Publication

Manaa, M. R. et al. Prediction of Extended Aromaticity for a Novel $C_{48}N_{12}$ Aza-Fullerene Structure. *Journal of the American Chemical Society* **2002,** *124,* 13990.

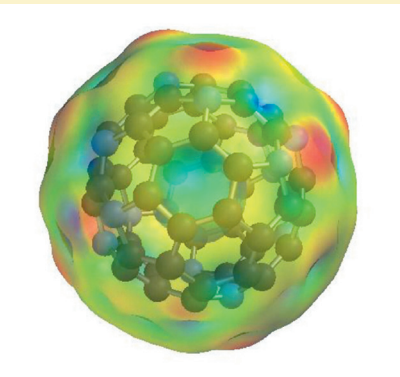

Figure 3. The molecular structure of $C_{48}N_{12}$, showing the electron-density clouds.

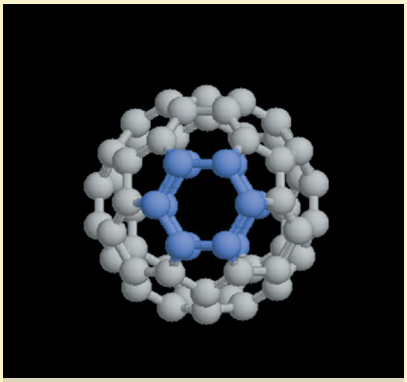

Figure 4. The high-energy structure of $C_{48}N_{12}$, with two benzene-like N_6 rings.

Author

K. Glaesemann

Related Publications

Glaesemann, K. R.; Fried, L. E. Improved Heat Capacity Estimator for Path Integral Simulations. *Journal of Chemical Physics* **2002,** *117,* 3020.

Glaesemann, K. R.; Fried, L. E. An Improved Thermodynamic Energy Estimator for Path Integral Simulations. *Journal of Chemical Physics* **2002,** *116,* 5951.

Glaesemann, K. R.; Fried, L. E. A Path Integral Approach to Molecular Thermochemistry. *Journal of Chemical Physics* **2003,** *118,* 1596.

Understanding Energetic-Material Response

Energetic materials (e.g., explosives, propellants, and pyrotechnics) function by rapidly releasing large amounts of energy. Before we can predict the response of systems that contain these materials, we must first understand the response of energetic materials to various stimuli. Our interdisciplinary approach to this difficult problem provides insight into energetic-material response by combining experimental studies using different length scales, from nanometers to meters.

Relevance to CMS Research Theme

This work, which is of the utmost importance to the Laboratory's stockpile stewardship mission, incorporates new developments in the emerging science of chemistry under extreme conditions. Our approach to developing predictive models for energetic-material systems involves a new, science-based methodology. Through the use of cutting-edge tools, such as the coupled thermal–chemical–mechanical hydrodynamics code ALE3D, and new measurement techniques to determine material properties at extreme temperatures and pressures, our work is furthering the science of material response.

Major Accomplishments in 2002

Tetranitrotetrazacyclooctane (HMX) is one of the most commonly used energetic materials. Our scientific understanding of the behavior of HMX-based explosives has significantly matured in 2002. From our investigations of HMX behavior when HMX is heated to the point of explosion, we have quantified the deflagration behavior and shock response of several HMX-based explosives when heated and have begun to develop model descriptions that can be incorporated into continuum codes such as ALE3D.

We have also completed a series of quantitative thermal-explosion experiments and are using them to validate the models in ALE3D. In addition, the solid–solid phase transition in HMX has been studied and is being incorporated into our models.

Most energetic materials contain polymeric binders in addition to energetic crystals such as HMX. Our polymer studies have focused around issues of crystallinity. We have performed the first atomistic simulations of bulk polymer crystallization. These simulations, which require the use of hundreds of processors for several months, have resulted in a unique understanding of the initial events controlling polymer crystallization and have enabled us to identify the nucleation and growth regimes in polymeric materials for the first time (Figure 1). This research has provided us with mission-relevant insight into the aging of materials, as well as fundamental knowledge about

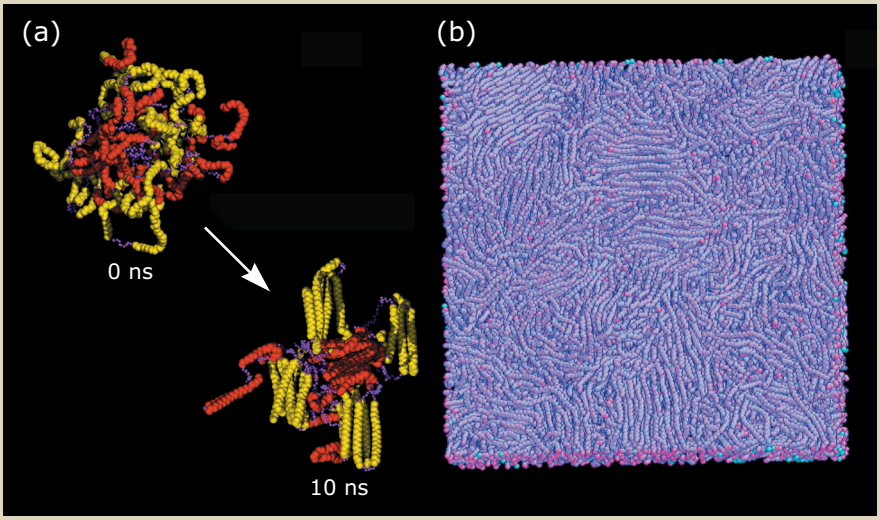

Figure 1. (a) Simulation of crystal growth for the poly(vinylidene fluoride) polymer during a time interval of 0 to 10 nanoseconds. (b) A 1000-chain ensemble illustrating the polymer's polycrystalline nature.

the nature of polymer crystallization and growth.

During the brief instant of a high-explosives detonation, the shock wave produces a pressure 500,000 times that of the earth's atmosphere. This detonation wave travels as fast as 10 kilometers per second, and internal temperatures soar up to 5500 kelvin. At present, computer simulations provide the best access to the decomposition processes occurring in these regions of extreme pressure and temperature at very short time scales.

We have modeled these processes by conducting ab initio based molecular dynamics simulations of highly compressed energetic materials at constant high temperatures in the range of 2500 to 5000 kelvin. Following the reactivity of the dense fluid for reaction times up to a hundred picoseconds enables us to construct reaction-rate laws for the formation of stable products, such as water, nitrogen, carbon dioxide, and other species. These simulations have provided us with atomistic insight into the chemical reactivity of energetic materials for the first time.

Future Goals

Our overall goal is to further the understanding of energetic materials through a science-based, interdisciplinary approach spanning multiple length and time scales. To achieve this, we are incorporating improved physical and chemical models into continuum codes such as ALE3D. These models are, in turn, based on state-of-the-art experimentation and modeling. Further development of our experimental capabilities through direct in situ probes of dynamic processes will greatly enhance our understanding of energetic-material properties and response.

Authors

L. Fried, R. Gee, J. Maienschein, M. Manaa, M. McClelland, and A. Nichols III

Related Publications

Gee, R. H.; Fried, L. E. Ultrafast Crystallization of Polar Polymer Melts. *Journal of Chemical Physics* **2003,** *118,* 3827.

Manaa, M. R. et al. The Decomposition of HMX at Extreme Conditions: A Molecular Dynamics Simulation. *Journal of Physical Chemistry A* **2002,** *106,* 9024.

New Frontiers

The properties of energetic materials vary greatly between pristine material and that which has been degraded through thermal, mechanical, or chemical means. A new thrust in this program is characterizing damaged and aged energetic materials and understanding their underlying chemistry and physics.

This work represents a new focus area in experimental modeling. Figure 2 shows a computer simulation of the extremely violent response of a slowly heated annulus containing a damaged HMX explosive. The unique coupling of chemistry, thermal transport, and hydrodynamics in ALE3D is necessary to describe such events.

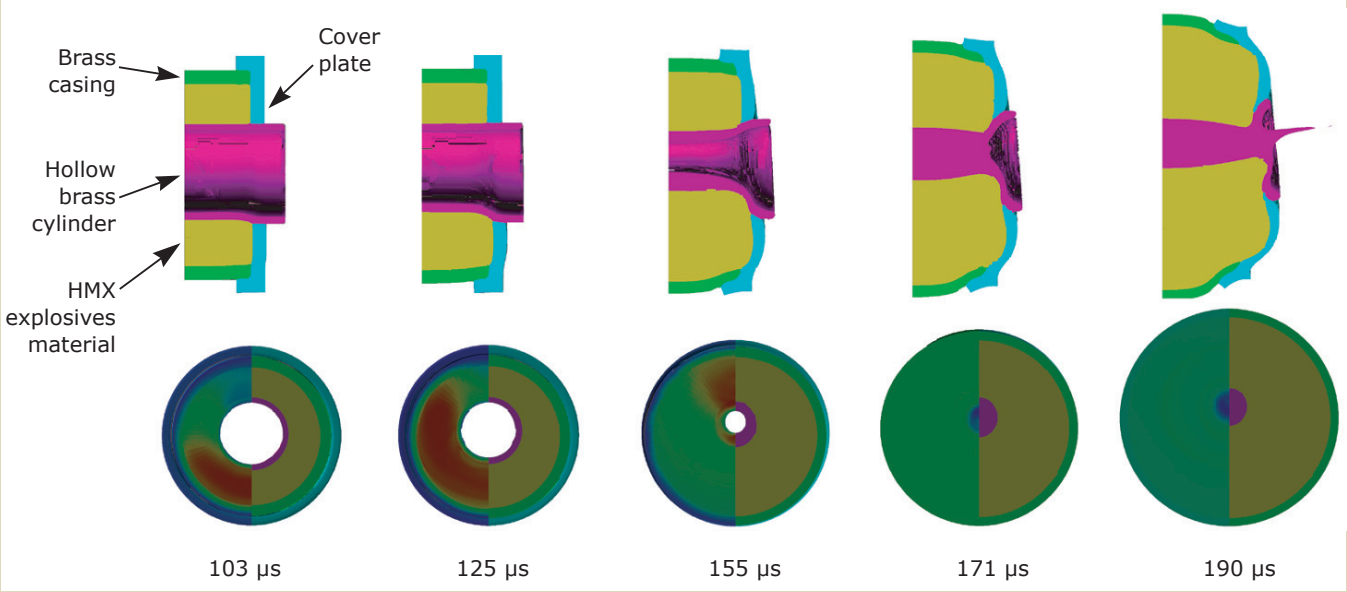

Figure 2. An ALE3D simulation of the response of a heated, symmetrical high-explosive device at a short time (103 to 190 microseconds) after ignition. At each time interval, the top image shows a cutaway of the device along the vertical axis, and the bottom right shows a cutaway along the horizontal axis. The colors in the bottom left show the amount of pressure in the device. Cooler colors (blue, green) indicate lower pressure; warmer colors (yellow, orange) indicate higher pressure, and areas of peak pressure are red.

Carbon Nanotube Arrays for Novel Molecular Separation and Concentration Devices: Nanofilters, Nanomembranes, and Nanopores

To combat bioterrorism, we will need small "smoke detector" type devices that can rapidly identify potential biohazards in the field. These devices must be created using microfabrication techniques to reduce device size, cost, and energy consumption. However, because such detectors need relatively clean samples to detect and identify bioagents, the detectors will require an effective mechanism for molecular separation and concentration.

Although current microfabrication techniques can create channel networks for transporting, mixing, and sampling solutions, these techniques cannot be used to fabricate separation and concentration elements that contain patterned materials of predetermined surface properties, geometries, and porosities at the molecular scale. Further refinement and miniaturization of separation and concentration technologies can only be achieved by using unconventional materials and fabrication strategies.

Relevance to CMS Research Theme

Our project supports the Laboratory's national-security mission by developing new separation and concentration technologies to combat bioterrorism, a key threat to homeland security. Specifically, our research uses patterned arrays of carbon nanotubes (CNTs) to create a new class of separation and concentration elements that can easily be incorporated into microfabricated gas- or liquid-phase devices. These elements are built by using template-directed nanotube synthesis inside prefabricated microfluidic channels.

CNTs are graphite sheets rolled up into thin tubes that measure less than 200 micrometers in length, while still maintaining a diameter of 1 to 20 nanometers. Because of their unique geometry and physical properties, CNTs show great potential as a new collection-element material. For example, the phenomenally high surface-to-volume ratio of a nanotube mesh makes CNTs naturally suited for collection and separation applications. In addition, the curved surface of a CNT has a high surface energy, which facilitates the attachment of species to the CNT surface.

Major Accomplishments in 2002

The main challenge in bringing the promise of nanotube arrays to life is incorporating the arrays in workable device architectures. We chose to use catalytic chemical vapor deposition (CVD) to fabricate our nanotube arrays for several reasons: (1) CVD enables us to control nanotube placement by simply patterning the catalyst (Figures 1a and 1b); (2) CVD growth conditions are compatible with devices microfabricated in silicon or quartz; and (3) CVD growth is easily scalable, so many devices can be grown in parallel on a full wafer scale.

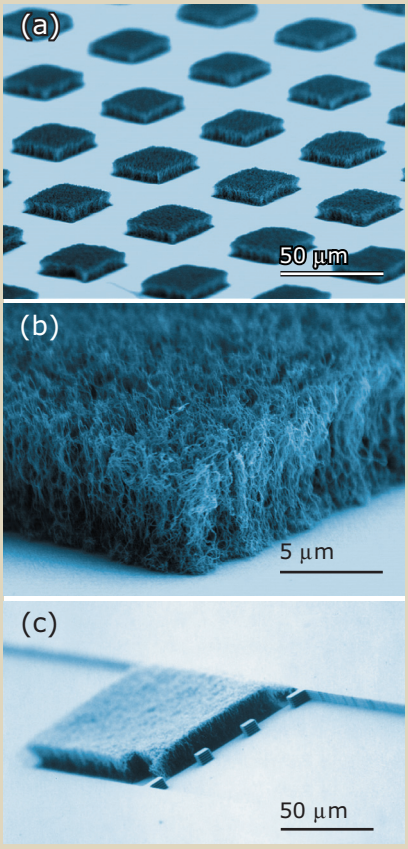

Figure 1. Patterned carbon nanotube arrays. (a) A typical forest of nanotube patches. (b) A close-up of a patch. (c) A nanotube patch grown inside a microfluidic channel.

Under optimized growth conditions, we were able to use a catalyst to grow dense uniform nanotube arrays across our channels (Figure 1c). The channels were then capped with glass cover slips using anodic bonding in an inert atmosphere. The finished devices were fully compatible with standard microfluidic testing equipment.

To demonstrate the filtration capability of our devices, we pushed a solution containing fluorescent beads through a device that had a nanotube mesh element spanning the channel's cross section. The element successfully captured a significant portion of the beads (Figure 2).

We demonstrated that our nanotube elements can be used to perform chromatographic separation. Specifically, we used different solvents to force the capture and subsequent removal of beads from the nanotube surface and noted that this type of separation is better performed in channels where the nanotube element spans only part of the channel's cross section.

Future Goals

We are refining the CNT fabrication strategy. In addition, we plan to test nanotube surface-modification strategies to understand the fundamental physical principles that govern molecular adhesion to CNT surfaces. This research will enable us to develop efficient collectors and help us understand and manipulate collection specificity.

We are also exploring the use of CNTs to fabricate a new class of nanoporous membrane materials. These membranes could be used for chemical and biological sensing or for studying molecule motion through a straight ideal pore. Furthermore, we are developing strategies for interfacing these membranes with biological and chemical sensors.

In addition, we are exploring the use of isolated CNTs as molecular-scale sensors that feature detection selectivity. We are developing a synthetic strategy to coat CNTs with defined lipid membranes. We can then define membrane porosity by introducing the appropriate protein channels. The development of this technology will move us closer to a biological smoke detector.

Authors

A. Noy, O. Bakajin, D. Eaglesham, and S. Létant

New Frontiers

DNA Detection through Designed Apertures

The goal of this new project is to support the Laboratory's homeland security mission by demonstrating a fast and sensitive DNA signature detector that will be tested with anthrax and plague. Specifically, our project will demonstrate the selective detection of the DNA signatures of harmful organisms by using a rigid silicon aperture that mimics an ion channel. Our long-term goal is to build an array of apertures, with each able to detect the DNA of a specific organism.

Other research groups are also attempting to build a single nanopore on a rigid substrate, but our group's technique of using a single-probe DNA strand to functionalize the nanopore is unique. Our approach, which lies at the cutting edge of nanotechnology and supramolecular chemistry, should transform synthetic nanopores into extremely selective sensors. If successful, our project will create a new class of biosensors able to detect and identify DNA signatures from harmful organisms with single-molecule sensitivity. These detectors would greatly improve our nation's early response to the biological contamination of air or water.

CMS Contact: S. Létant

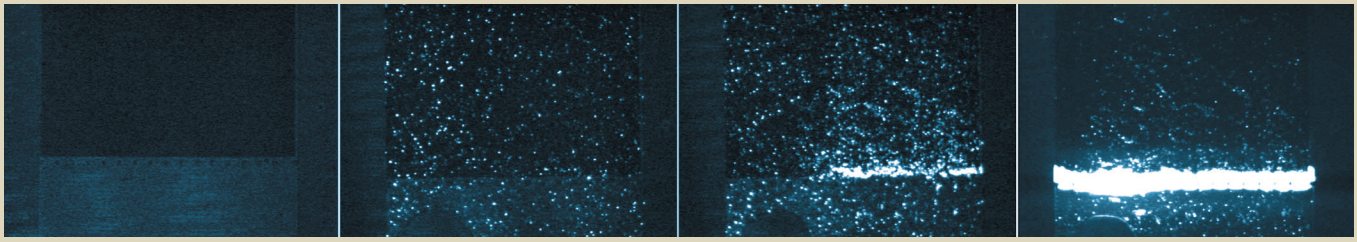

Figure 2. Time-lapse images (left to right) showing the collection of fluorescent beads (the bright dots) at the front edge of a nanotube mesh element that is being used as a filter.

Multiscale Computational Chemistry: Modeling of Aerosol and Combustion Chemistry

Large-scale computational science, which was invented at Livermore, continues to be a fundamental research tool for multiple classes of projects. Many Laboratory programs require the modeling of complex systems, so the computational tools being developed here are applicable to a wide range of problems.

CMS computational chemists are able to tackle extremely challenging technical problems using the world's most powerful, massively parallel computers, which were recently acquired through the Laboratory's Advanced Simulation and Computing (ASCI) Program. During the past year, our research group has made important contributions to programmatic directorates, including Defense and Nuclear Technologies; the National Ignition Facility (NIF); Nonproliferation, Arms Control, and International Security; and Energy and Environment. We have also used our computational tools to investigate fundamental problems in biology.

Relevance to CMS Research Theme

Multiscale computational problems are common in CMS research. These problems couple vastly different time scales or subsystems to model the effects of atomistic evolution in the macroscopic features of a larger system.

Examples of ongoing research topics involving such problems include damage mechanisms in metals and other stockpile stewardship materials, NIF laser glass, energetic materials and high explosives, the performance of practical energy systems, and the molecular evolution of biological systems important to national security. Significant advances in solution techniques will simultaneously impact these ongoing studies, which are among the many CMS research projects conducted in support of national objectives at the intersection of chemistry, materials science, and biology.

Major Accomplishments in 2002

Recent improvements in computer hardware and numerical algorithms have made it possible to include many more atoms and larger domains for molecular dynamics (MD) simulations, thereby greatly reducing the uncertainties in extrapolating computed results to realistic problems.

A new computational formulation coupled MD with kinetic Monte Carlo (KMC) to study how postflame hydrocarbons evolve to produce soot

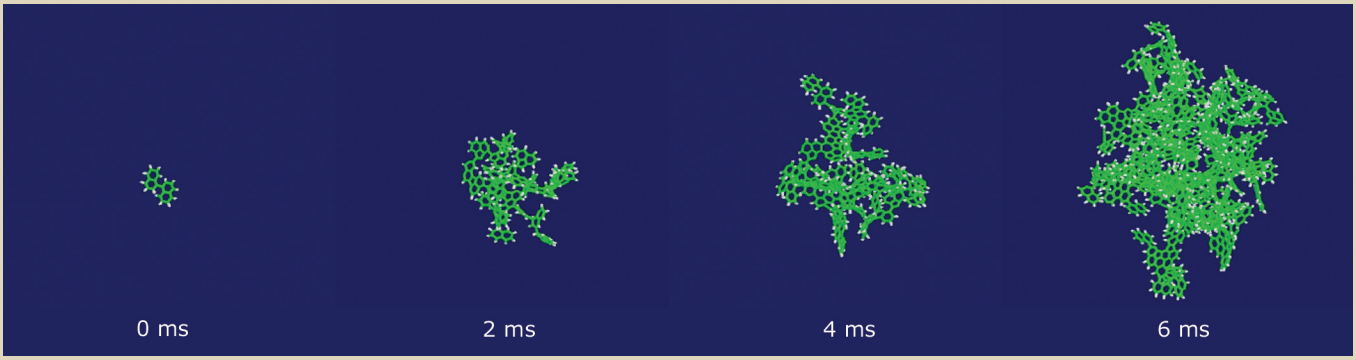

Figure 1. Four snapshots showing the growth of a soot particle from a small, four-ring, gas-phase aromatic compound to a large, polymerized molecule ready to condense into a solid soot particle.

in diesel engines and flames. MD was used to achieve local equilibrium over very short time scales, while KMC was used to predict reactions that take place over time scales many orders of magnitude longer than those for the MD simulations.

Figure 1 shows a model that combined MD and KMC analyses to depict the evolution of a growing soot particle. Dozens of elementary reactions in the KMC analysis increased the size of the soot particle, while MD changed the structure of the particle between reactions.

Other applications of this same capability have included studies of laser-glass damage mechanisms and of the aging of metals over long periods of time. Additional new MD studies of energetic materials and biological systems conducted this past year included the first computational demonstration of rapid crystallization in bulk polymers.

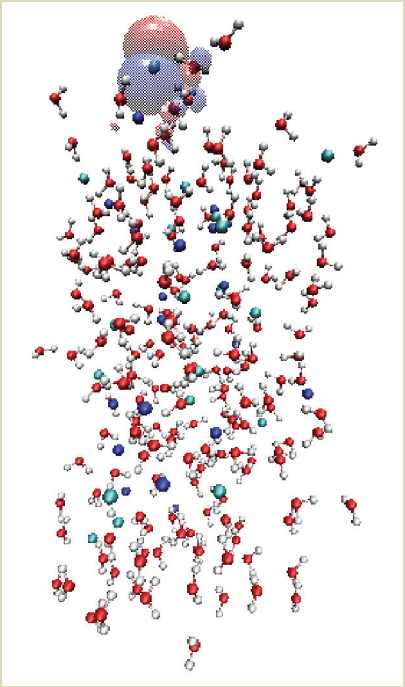

Figure 2. The highest-occupied molecular orbital (HOMO) of the sea-salt interface. The blue-green balls denote chloride ions; the dark blue balls represent sodium ions; the red balls are oxygen atoms, and the white balls are hydrogen atoms. The translucent red and dark blue iso-surface represents the different phases of the wave function. The HOMO lies on the surface chloride atom.

We also conducted a major series of ab initio MD simulations that examined the nature of the liquid–gas interface at the surface of aerosol droplets. Droplets that formed around sea salt were shown to push chloride ions preferentially to the droplet surface, thereby altering the reactivity for gas-phase molecules such as nitric acid and other pollutant molecules. Figure 2 shows the highest-occupied molecular orbital for a saturated sea-salt interface. The figure suggests that the reactivity of the interface is dominated by undercoordinated chloride ions, a result corroborated by experiments. Additional studies examining the surface of pure-water droplets suggested that dangling hydrogen bonds are present at the surface.

Further kinetic modeling research provided reaction mechanisms for the combustion of large hydrocarbon fuels characteristic of practical transportation fuels (e.g., gasoline, diesel, and jet fuels). These models helped to screen new fuels that may reduce diesel engine soot and eliminate groundwater pollution from gasoline additives such as methyl tert-butyl ether (MTBE). Similar efforts examined reaction pathways unique to chemical-warfare nerve agents such as Sarin and VX.

Future Goals

We will continue to pursue basic-science problems investigating the fundamental structure of liquid–gas interfaces, particularly in aerosols involving water. Additional planned studies include charge transfer and other reactions in amino acids and biological systems. We will also continue our energy-systems study of the evolution of soot and other particulate matter.

New Frontiers

Our multidimensional and multiscale approach will be used to develop more economical models to study the evolution of chemicals and aerosols in the atmosphere—problems that have important applications in air pollution, chemical warfare, and energy policy. The approach will also be used to advance programmatic applications such as studies of laser-glass damage relevant to NIF, nanostructured materials involved in fusion and fission reactor vessels, and metal aging related to stockpile stewardship.

Future applications require that we continue to stretch the capabilities of current supercomputing resources to include more atoms, larger scales of time and distance, and more complexity in chemical simulations. To do so, we will need to improve our algorithms for multiscale problems and develop more imaginative formulations of supercomputing problems.

Authors

C. Mundy, C. Westbrook, and A. Kubota

Related Publications

Gee, R. H.; Fried, L. E. Ultrafast Crystallization of Polar Polymer Melts. *Journal of Chemical Physics* **2003,** *118,* 3827.

Mundy, C. J. et al. Irradiated Guanine: A Car-Parinello Molecular Dynamics Study of Dehydrogenation in the Presence of an OH Radical. *Journal of Physical Chemistry* **2002,** *106,* 10063.

Violi, A. et al. A Fully Integrated Molecular Dynamics—Kinetic Monte Carlo Approach for the Simulation of the Growth of Soot Precursors. *Proceedings of the Combustion Institute,* in press.

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Scanning Probe Nanolithography for Controlled Protein Deposition

The goal of deterministically collecting and organizing atoms, molecules, nanoparticles, and cells into ordered arrays at surfaces has enormous potential for materials science, synthetic chemistry, biology, and medicine.

In recent work at Livermore and elsewhere, scanning probe microscopes have been used to create patterns of surface chemistry with feature sizes below 50 nanometers. Other studies have shown that such patterns can act as templates of the surface and interfacial energies, thereby controlling deposition and crystallization. Our research combines these two concepts to develop methods for patterning macromolecular deposition into ordered arrays and then using the patterns to probe the interactions that drive macromolecular assembly at surfaces.

Relevance to CMS Research Theme

This nanoscience research, which is at the intersection of chemistry, biology, and materials science, has the potential to impact the Laboratory's national-security mission as well as fundamental and applied missions in biology and materials science. For example, the ability to create nanometric chemical templates can lead to the fabrication of high-density DNA and protein chips for biodetection and high-throughput assays. More significantly, a generic route for creating molecularly ordered protein arrays will revolutionize protein atomic-structure determination by eliminating the need for crystallization. In addition, because the chemistry used to deterministically locate individual macromolecules can be applied to the scanning probe tip, this method provides a platform for directly measuring the force of interaction between proteins, antibodies, and other macromolecules.

Major Accomplishments in 2002

Two scanning-probe-nanolithography methods have been developed for creating nanometric chemical patterns (Figure 1). Figure 2 illustrates dip-pen nanolithography, which patterns gold and silicon oxide surfaces at 10-nanometer length scales. After dipping into a chemical, or "ink" (e.g., laser dyes, photoluminescent polymers, or antibodies), an atomic force microscopy (AFM) tip moves in a predetermined pattern across a substrate. The substrate then reacts with a second ink to create a background with a different chemistry.

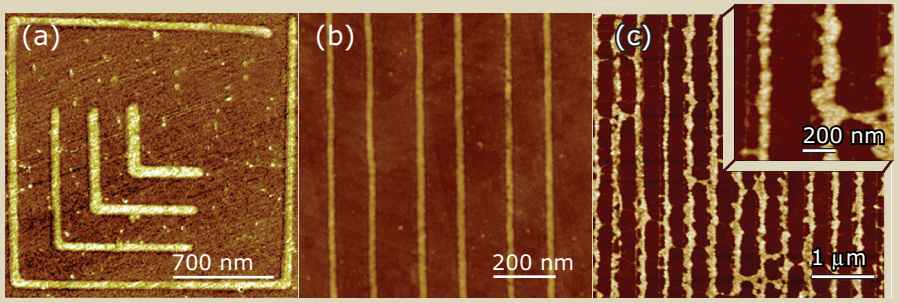

Figure 1. Atomic force microscopy images of patterns formed by (a) dip-pen nanolithography using carboxyl-terminated alkane thiol dots on gold, (b) nanografting using amino-terminated ink, and (c) nanografting using chemoselective linkers. In (c), individual virions (visible in the higher-resolution inset) have self-assembled on the pattern, forming a monolayer.

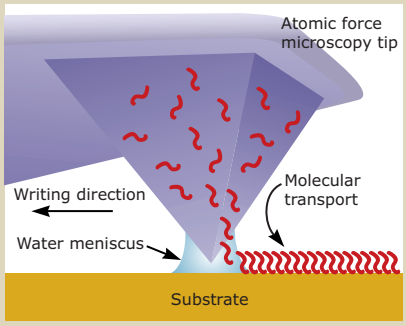

Figure 2. The dip-pen nanolithography process: An atomic force microscopy tip that has been dipped into a chemical (the "ink") "writes" on a substrate by moving across the surface. The ink diffuses from the tip through the water meniscus to the surface.

In the second method, nanografting, the substrate is covered with an ink, forming a self-assembled monolayer. The AFM tip removes the ink in a predetermined pattern. The substrate then reacts with a second ink, which self-assembles to fill in the pattern.

Both methods were used to develop a generic approach to templating macromolecular deposition (Figure 3): (1) A macromolecule is genetically engineered to express a reactive chemical group (e.g., a thioester or sulfhydryl group) at a specific site on the molecule's surface. (2) Long-chain alkane molecules are synthesized as inks that self-assemble on either gold or silicon oxide surfaces. The molecules present a head group, which reacts covalently with the modified site. (3) A scanning-probe-nanolithography method is used to create a pattern of this ink within a background, which provides a polyethylene glycol functionality that resists protein binding.

We chose the cowpea mosaic virus (CPMV) as a model macromolecular system because its 29-nanometer diameter is well-suited for patterning by scanning probe nanolithography and because CPMV can be engineered to express sulfhydryl groups at specific sites on the surface capsids (Figures 4a and 4b). We then used nanografting to pattern CPMV deposition with amino-terminated inks in a polyethylene-glygol-terminated background (Figure 4c). Successful control over deposition is demonstrated in Figure 1c.

Future Goals

We plan to (1) explore a range of virus concentrations and solution conditions to maximize the degree of order in the patterns; (2) directly measure the virus–substrate and virus–virus interaction forces for input into kinetic Monte Carlo codes of assembly; and (3) expand this work to the two dominant protein classes: globular and membrane. For a globular protein system, we have chosen the SH3 domain of the Crk DNA repair protein, which has been engineered to express a thioester group at its C-terminus. We have already demonstrated controlled deposition at the micrometer scale on patterns of an ink designed to bind to the modified site. The next step is to pattern the ink with scanning probe nanolithography.

New Frontiers

The thousands of proteins encoded within the human genome hold the key to understanding cellular function. Protein structures are currently determined through x-ray diffraction of bulk single crystals. However, protein crystallization is a difficult task. At present rates, obtaining single crystals of every protein expressed by the human genome would take about 100 years.

A generic method for patterning protein deposition by using scanning probe nanolithography would open a new frontier in this field. Ordered arrays of proteins could then be probed with synchrotron sources to determine atomic structures, eliminating the need to grow bulk crystals. For example, rows of proteins could pass through a superbright synchrotron beam. A diffraction pattern would then be produced for each protein so that its full 3-D atomic structure could be reconstructed.

Authors

J. De Yoreo, B. Weeks, C. Cheung, J. Camarero, A. Noy, and B. Woods

Related Publications

Cheung, C. L. et al. Fabrication of Assembled Virus Nanostructures with Chemoselective Linkers by Scanning Probe Nanolithography. *Journal of the American Chemical Society,* in press.

Weeks, B. L. et al. Effect of Dissolution Kinetics on Feature Size in Dip-Pen Nanolithography. *Physical Review Letters* **2002,** *88,* 5505.

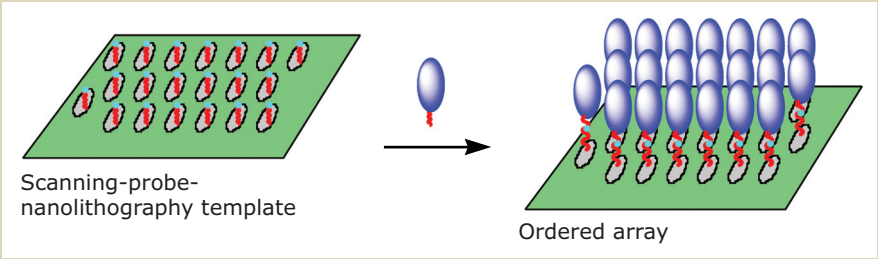

Figure 3. A schematic of the generic approach to templating macromolecular deposition. The macromolecules are genetically engineered to present a functional group that will bind to the head group of a self-assembled monolayer deposited by scanning probe nanolithography.

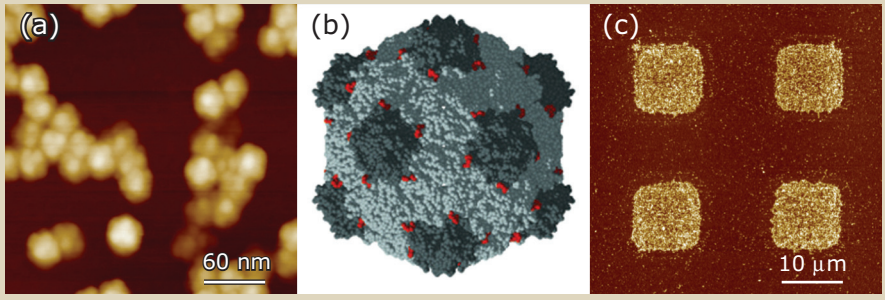

Figure 4. (a) An atomic force microscopy (AFM) image of the cowpea mosaic virus (CPMV). (b) A model of Cys-CPMV, with the genetically mutated cysteine residues in red. (c) An AFM image of Cys-CPMV showing specific binding to a micrometer-sized template formed by a contact printing method.

Single-Cell Proteomics with Ultrahigh-Sensitivity Mass Spectrometry

The quest to understand biological systems is an enduring goal in modern science. Because biological systems are fundamentally composed of single cells, new tools for analyzing single cells must be developed. As these tools mature, we will be better equipped to understand, detect, and curtail the spread of disease due to both natural causes and the intentional use of biological weapons.

Our research group is developing a technique for analyzing the molecular composition of single cells with potential applications for both biological defense and biomedical research. This high-throughput, real-time, reagentless technique is called bioaerosol mass spectrometry (BAMS) and is based on laser ionization time-of-flight mass spectrometry (TOF-MS). BAMS identifies individual cells by measuring proteins and other biomolecules in single cells (Figure 1) and will be used to study the molecular changes in these cells during their normal and abnormal growth and death.

Relevance to CMS Research Theme

CMS is dedicated to developing the nanoscale biological analysis tools required to drive the evolution of biosensors for national-security and medical-diagnostics applications. Our work with BAMS is a valuable addition to this continuing effort within CMS. For example, the BAMS technique can be used as a national-security tool to detect bioagents in both civilian and military settings. BAMS also has several potential biomedical applications, such as detecting cancer by analyzing individual cells in clinical biopsies and providing noninvasive symptomatic and presymptomatic diagnoses by

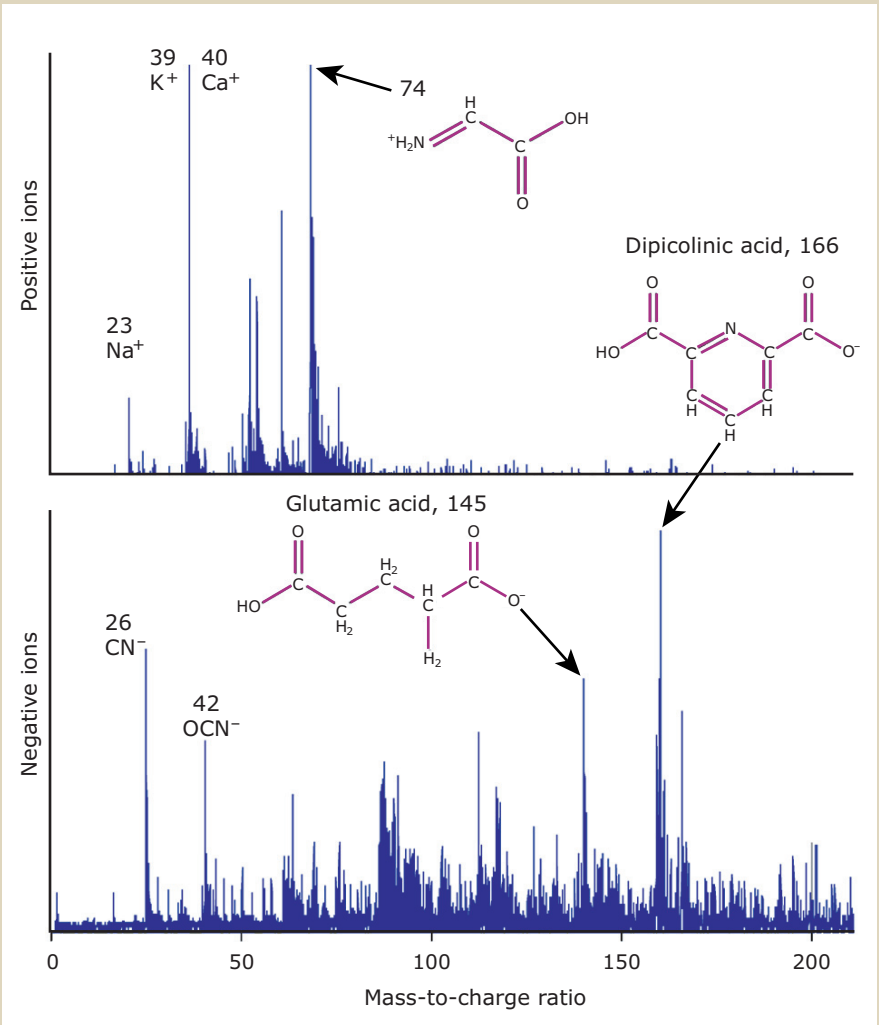

Figure 1. The mass spectrum of a single bacterial spore. Mass spectrums are used by the bioaerosol mass spectrometry system to identify individual cells.

analyzing respiratory effluents (coughs or sneezes). However, achieving these objectives will first require combining advanced laser desorption and ionization techniques with mass spectrometry to improve TOF-MS sensitivity and selectivity by 2–3 orders of magnitude.

Major Accomplishments in 2002

We have demonstrated that unique molecular signatures can be obtained from individual bacterial spores, enabling us to discriminate between bacteria and background aerosols. Because of these experimental results, the Department of Defense has expressed interest in using our technology for biological aerosol detection. In addition, we have implemented an infrared laser desorption and ultraviolet ionization experiment that has greatly increased BAMS's ion-generation capability (Figure 2).

Future Goals

Our goal is to develop a portable bioaerosol-detection instrument that can be used in the field to detect the entire spectrum of biological agents that are of concern to national security. We also wish to expand the BAMS technique for use in medical diagnostics and hope to partner with industry to develop a commercially available detection instrument.

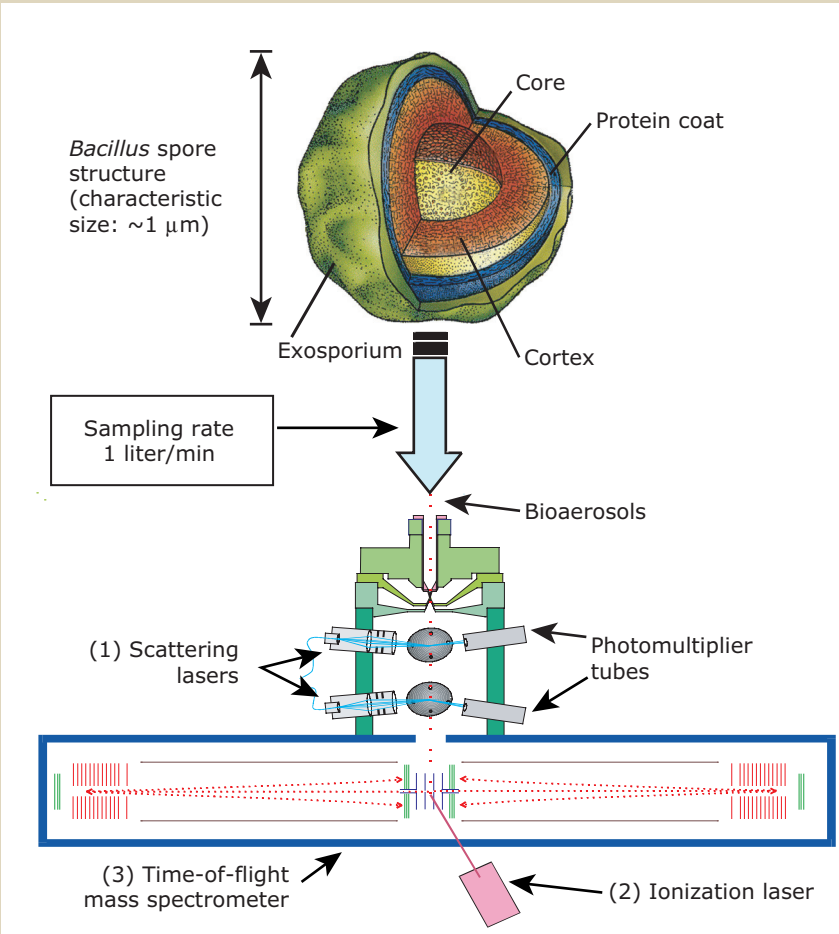

Figure 2. A cutaway diagram of a bacterial spore (top). The schematic shows how spores are sampled into the bioaerosol mass spectrometry system: (1) Two scattering lasers track individual cells. (2) A high-power laser ionizes single cells. (3) The ions are analyzed by time-of-flight mass spectrometry to identify the molecular weight of each cell.

New Frontiers

Our work will demonstrate the use of single-cell mass spectrometry for studying cellular processes. After we increase the sensitivity of TOF-MS by combining aerosol mass spectrometry with advanced laser desorption and ionization techniques, we will work on implementing the national-security and medical-diagnostics applications of BAMS.

The first application to be examined is the relationship between mass signatures and cell viability when cells are affected by radiation damage. We also plan to expand our studies of the influence of laser wavelength on signatures to include short-pulse lasers.

Author

E. Gard

Related Publications

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Steele, P. T. et al. Laser Power Dependence of Mass Signatures from Individual Bacterial Spores in Bioaerosol Mass Spectrometry. *Analytical Chemistry,* in press.

Heavy Element Discoveries: Elements 114 and 116

Since 1989, our research group has collaborated with scientists from the Flerov Laboratory of Nuclear Reactions in the Joint Institute for Nuclear Research in Dubna, Russia. Our goal has been to search for and map out regions of enhanced nuclear stability against decay by spontaneous fission.

In 1998, encouraged by the collaboration's past success in mapping the hexadecapole-deformed region of stability centered at element 108, we decided to search for the long-sought "island of stability" of superheavy elements. On November 22, 1998, during the bombardment of plutonium-244 with calcium-48 ions at the U400 cyclotron, we arrived at the edge of the island of stability by producing one atom of 114-289 (the element 114 isotope with a mass number of 289). This atom had an amazingly long lifetime of 30 seconds. Subsequent bombardments of plutonium-244 with calcium-48 produced two atoms of 114-288 with a half-life of about 2 seconds. The signature of the production of these isotopes was an α–decay sequence that was terminated by spontaneous fission as the boundary of the stable region was left behind.

In 2000, we irradiated curium-248 with calcium-48 in an attempt to produce isotopes of element 116 that would be the α-decay parents of the element 114 isotopes. During the course of the irradiation, we observed three atoms of 116-292 decay into the element 114-288 chain. The observed decay chains were consistent with the previously measured decay properties of 114-288.

Relevance to CMS Research Theme

The extension of the heavy end of the chart of the nuclides has been one of the most exciting aspects of nuclear chemistry and nuclear physics in the last 50 years. Thanks to our work, new-element discoveries are once again prominently in the scientific spotlight.

Efforts to synthesize new elements and isotopes and measure their nuclear-decay properties are essential for CMS to maintain its core competency in nuclear chemistry and radiochemistry. This expertise is needed by Laboratory programs to assist them in carrying out their missions.

For example, nuclear and radiochemical expertise is provided to the Defense and Nuclear Technologies Directorate to help understand and diagnose the performance of nuclear explosive devices; to the Nonproliferation, Arms Control, and International Security Directorate to identify and diagnose possible proliferant activities involving nuclear materials; and to the Energy and

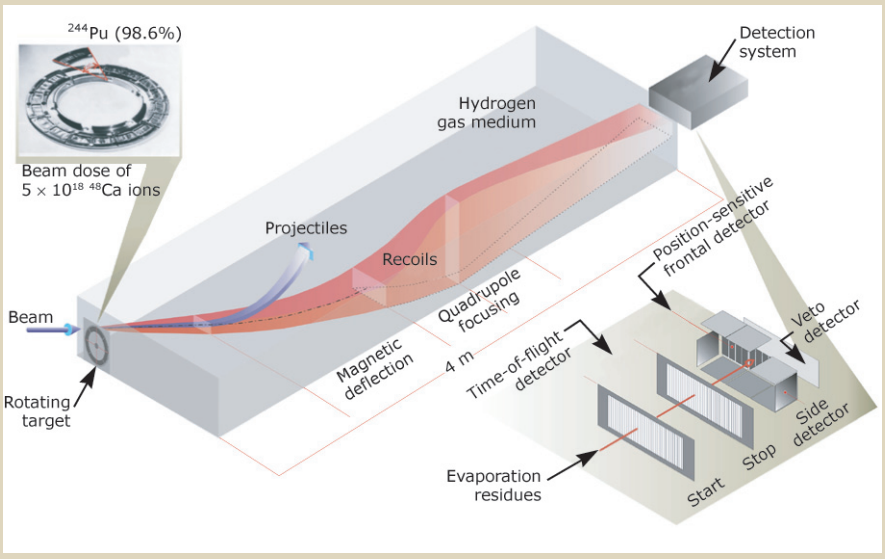

Figure 1. A schematic of the Dubna Gas-Filled Recoil Separator, which was used in isotope studies of elements 114, 116, and 118 to suppress unwanted reaction products.

Environment Directorate to help understand issues related to nuclear power production and the safe disposal of radioactive materials.

Major Accomplishments in 2002

We have continued to investigate the topography of the western edge of the island of stability by bombarding californium-249 (half-life of 351 years) with calcium-48 ions at the U400 cyclotron. The goal of this experiment is to synthesize element 118, which has not yet been discovered. The decay daughters of element 118 will be isotopes of elements 114 and 116 that have also not yet been discovered. The properties of element 118 will help to further define the extent of the island of stability.

The experiment is being performed with the Dubna Gas-Filled Recoil Separator (Figure 1). In the course of a 2300-hour irradiation of a californium-249 target (0.23 milligrams per square centimeter) with a beam of 245-MeV calcium-48 ions, we have accumulated a total beam dose of 2.5×10^{19} ions.

We have also detected two events that may be attributed to the formation and decay of an element 118 isotope. For one event, we observed a decay chain of two α decays terminating in spontaneous fission, which occurred over a time interval of 0.52 second. In the second event chain, the recoil nucleus decayed into two fission fragments 3.16 milliseconds later, without intervening α decays. The decay characteristics of the newly observed nuclides are comparable with the calculations made in various nuclear models.

Future Goals

In the next year, we plan to irradiate a target of americium-243 with calcium-48 ions to produce element 115 and possibly, by subsequent α decay, a second new element—element 113. From the expected reaction's cross section and our intended target thickness, we anticipate producing one atom of element 115 for every four weeks that the target is irradiated. The half-life predictions for element 115 nuclides are on the order of milliseconds, which is ideal for experiments at the gas-filled separator.

The spontaneous-fission and α-decay hindrance factors for nuclides with odd atomic numbers suggest that the signature for the decay of an element 115 isotope will be a two- or three-member α-decay chain, terminated by spontaneous fission when the decay leads to the edge of the region of stability. Since 115-288 is an isotone of the known isotope 114-287 (both have 173 neutrons), we may also have the opportunity to study the decay properties of nuclei with 173 neutrons and to directly probe the influence of the closed proton shell when the atomic number is 114.

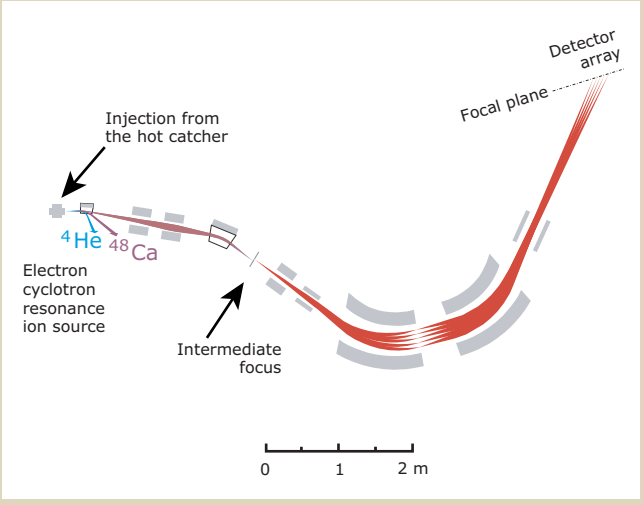

Figure 2. Schematic diagram of the electromagnetic part of the Mass Analyzer of Super Heavy Atoms (MASHA). Reaction products with masses near those expected for heavy-ion fusion products will be mass-analyzed by MASHA and delivered to the focal plane at well-defined positions.

New Frontiers

In the next year, we will participate in the construction and operation of a mass separator known as the Mass Analyzer of Super Heavy Atoms (MASHA). MASHA (Figure 2) will provide precise measurements of the atomic mass numbers of element 114 isotopes, including those that we discovered from 1998 to 2000. With the use of MASHA, the production rate of element 114 isotopes is expected to increase by a factor of 20, making further chemical and physical measurements possible.

The Laboratory is responsible for fabricating a plutonium ceramic target that will operate at temperatures approaching 2000 °C and for creating the front-end analog electronics that will be used in MASHA's detector system. We expect that experiments on MASHA at the U400 cyclotron will enable us to make measurements that will cement our identification of element 114 and pave the way for future experiments in which the chemical properties of the heaviest elements are studied.

Authors

K. Moody, J. Wild, M. Stoyer, N. Stoyer, C. Laue, D. Shaughnessy, J. Patin, J. Kenneally, J. Landrum, R. Lougheed, and the Flerov Laboratory of Nuclear Reactions Heavy Element Group

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Radiation Detection and Cargo Surveillance in Support of Homeland Defense

The attacks of September 11, 2001, and the subsequent anthrax bioterror incidents highlighted the vulnerability of the United States to assaults on its own land by highly organized and well-funded terrorist organizations such as al Qaeda. Even though these attacks were extremely costly in terms of loss of life, damage to property, and social impacts, the attacks of September 11 would be overshadowed in the event of a successful terrorist delivery and detonation of even a crude nuclear weapon on U.S. soil. Such an event—although horrific to imagine—must be prepared for, especially since al Qaeda reportedly has an interest in obtaining nuclear materials. There is also significant international concern about the possibility of nuclear weapons development in pariah states.

Because of the potential devastating capability of a nuclear weapon, the United States must develop systems to assure that such devices (and related terror weapons such as radiological-dispersal devices) cannot illicitly enter the United States without detection and interdiction. This is a major mission area of the new Department of Homeland Security that draws heavily on the Department of Energy's capabilities in radiation-detection systems.

Figure 1. A test of a handheld radiation detector with a cargo container of fissile material (plutonium). The other cargo containers in the transportainer contain materials similar to those that are typically shipped in international commerce.

Relevance to CMS Research Theme

CMS is supporting a major programmatic effort in the Nonproliferation, Arms Control, and International Security (NAI) and Homeland Security directorates to develop and field commercial-cargo traffic systems that can detect and identify illicit shipments of radioactive materials. As part of this program, we are testing existing technology against realistic nuclear materials (e.g., special nuclear materials [SNM]) in cargo

Figure 2. A ship passing through two ocean buoys at a U.S. Navy base. A system that can detect neutrons and gamma rays in water-based environments was placed on these two buoys.

containers, developing new methods and technology for detecting nuclear materials, and developing and installing prototype systems in field operations to guide further development. This work is conducted in close cooperation with stakeholders and first responders, including the U.S. Customs Service (USCS), the U.S. Coast Guard, the Transportation Security Agency, and state and local agencies. In addition, we are developing the next generation of radiation detectors for use in this arena, ranging from small, ultralow-power neutron detectors to state-of-the-art Compton imaging systems.

Major Accomplishments in 2002

We established a national intermodal cargo container test bed at the Laboratory's main site to provide a realistic challenge for commercial and prototype systems (Figure 1). At the test bed, we staged actual intermodal cargo containers that had typical cargo loads mixed with nuclear materials. We then tested every handheld or wearable commercial radiation detector under consideration by the USCS or the Coast Guard for field use. This test series provided critical performance data to USCS decision makers about the units, which included the pager-style radiation detectors now worn by every USCS field officer.

We also tested a mobile radiography system that is being procured by the USCS (at an approximate cost of $1 million per unit) to assess the system's ability to detect illicit nuclear material hidden within cargo containers. In collaboration with other Laboratory directorates (Engineering, Physics and Advanced Technologies, and NAI), we initiated a series of experiments to ascertain the absolute best performance of using neutron interrogation to detect weapons of mass destruction in cargo containers.

Future Goals

We wish to develop and deploy a system of commercially available detectors, supplemented by state-of-the-art prototypes of facilities maintained by the Port Authority of New York and New Jersey. The purpose of this operation will be to test the real-world performance of these detector systems. We will also test and refine protocols for responding to alarms that locate and identify illicit radioactive materials. Our goal is to ensure that responses to these detector alarms will not interfere with ongoing, legitimate commerce in radioactive materials (e.g., medical and industrial isotopes).

In addition, we plan to expand our existing collaboration with the Port of Oakland to detect illicit maritime commerce traffic in nuclear materials. We expect significant growth in this area as the Department of Homeland Security's program in nuclear and radiological counterterrorism evolves.

New Frontiers

Sensor Detector Systems

We have implemented a system that detects neutrons and gamma rays in water-based environments on two normal ocean buoys at a U.S. Navy base (Figure 2).

This system, which has a self-contained power supply and which uses wireless Ethernet to transmit data, was designed to test the usefulness of a variety of radiation detectors in a marine setting. Implementing the system on ocean buoys has the added benefit of enabling us to perform long-term measurements with a detection system that is in plain view.

Early-Detection Systems

Because screening for nuclear materials at port destinations may prove to be too late to avert disaster, a system is needed that would provide early warnings of nuclear materials before they arrive at their intended targets. Laboratory tests have demonstrated the possibility of detecting plutonium weapons of mass destruction within ship cargo containers. This means that early detection of nuclear materials can be provided through systems that combine long-term, real-time monitoring of neutron activity in cargo containers with advanced communication systems and electronics.

Figure 3 shows an inexpensive thermal neutron detector developed by our research group. When attached to a cargo container, this tiny detector can monitor incoming cargo shipments in real time. The neutron-detection efficiency of future detectors, which will monitor air cargo, will be 10 times higher than that of present detectors.

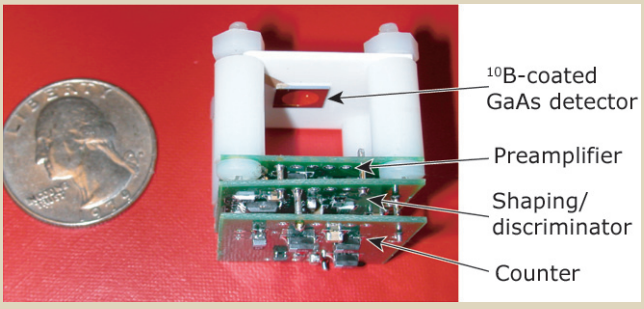

Figure 3. A tiny GaAs device coated with boron-10 that uses low-power electronics to detect neutrons in real time.

Authors
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The Bionuclear Research Initiative: Molecular Targeted Radionuclide Therapy

Initial projects in the CMS bionuclear initiative are aimed at using molecular targeted radionuclide therapy to cure advanced cancer. In this novel therapy, cancer-seeking molecules biologically deliver cytotoxic ionizing radiation to cancer throughout the body. The initiative seeks to improve (1) targeting agents, (2) subcellular pharmaceutical localization with secondary-ion mass spectrometry (SIMS), (3) cancer imaging, and (4) patient-specific radiation dosimetry. If successful, our research will advance the treatment of advanced cancer by changing how molecular targeted radionuclide therapy is prescribed and delivered.

Relevance to CMS Research Theme

The goal of the CMS bionuclear initiative is to bring together Livermore's expertise in nuclear and biomedical science to tackle problems in national security, health, and the environment in creative new ways. Each area of the initiative leverages existing Laboratory strengths with emerging technologies to create new links with the academic community, provide opportunities for growth and program development in national-security and civilian areas, and improve cancer care.

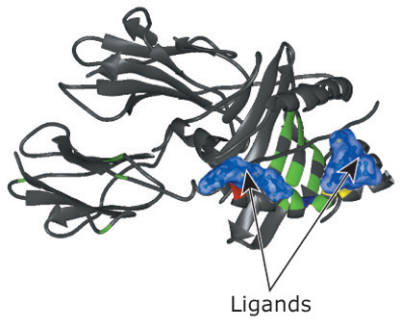

Figure 1. An HLA-DR10 protein, with two computer-selected ligands fitted into the protein's pockets.

Improved Targeting Agents

To develop synthetic high-affinity ligands (SHALs), a computer selects the ligands that best fit into two pockets on a target protein. The ligands are then linked with a lysine chain into a bidentate molecule. The resulting SHALs exhibit affinity with high specificity, potentially increasing the therapeutic index (the ratio of radiation dose in the tumor to the radiation dose in sensitive normal structures) by 10 to 100 times. Improvements of this magnitude are likely to raise the effectiveness of molecular targeting from causing cancer response to causing cancer cure. In addition, the SHAL concept is a key solution for the multiplexed detection of biological-warfare agents.

Major Accomplishments in 2002

Our first set of SHALs targets the mutated HLA-DR10 protein, which is present on lymphocytes and committed precursors in most non-Hodgkin's lymphoma patients. More specifically, the SHALs seek the epitope targeted by the successful Lym-1 monoclonal antibody. Figure 1 shows the targeted portion of the HLA-DR10 protein, with the computer-designed SHALs.

We synthesized our first SHALs targeted against non-Hodgkin's lymphoma and botulism toxin. We also tested our SHALs against non-Hodgkin's lymphoma. In a competition assay, our prototype SHAL was found to inhibit binding of the Lym-1 antibody.

Future Goals

We plan to measure each SHAL's binding affinity for the HLA-DR10 protein and test our SHALs on tissue arrays containing both normal and lymphoma cells. Depending on our findings, we will work to either improve SHAL performance or to test successful SHALs in mice for toxicity and therapeutic index. We will also refine the SHAL design, continue our testing on tissue arrays and mice, and prepare for clinical trials at the University of California (UC) Davis Medical Center.

Subcellular Pharmaceutical Localization with SIMS

SIMS combines mass spectrometry and focused ion-beam sputtering to provide ultrahigh sensitivity with micrometer-to-nanometer spatial resolution. SIMS will help elucidate the microscopic basis for observed pharmacokinetic properties in critical, dose-limiting organs. Our

studies are developing (1) biological-sample preparation techniques for analysis in the high-vacuum SIMS environment without altering in vivo chemical and isotopic distributions and (2) algorithms for converting secondary ion images into element and isotope distribution maps.

Major Accomplishments in 2002

We obtained our first SIMS images of pharmaceutical distributions for an yttrium-labeled 13 kDalton decapeptide distribution in a mouse kidney (Figure 2). These images showed that the yttrium is localized in the cells surrounding open (presumably tubular) spaces. This finding supports the hypothesis that renal retention of radiometals such as yttrium occurs through microscopic localization in the renal tubular cells. We also installed our new Cameca NanoSIMS, which provides a 40 times improvement in lateral resolution and a 10 times increase in sensitivity over our existing SIMS instrument.

Future Goals

We will use the NanoSIMS to explore why, at a subcellular level, molecular targeting agents tagged with radiometals (e.g., yttrium-90 and copper-67) have longer pharmacokinetic lifetimes in tumors and normal tissues than when tagged with iodine.

Improved Cancer Imaging

By leveraging programmatic investments in Compton imaging, we are designing a diagnostic system of radioisotope-tagged molecules and gamma-ray imaging. This system will improve the sensitivity and accuracy of imaging using molecular targeted radioisotope imaging agents. Our system will also demonstrate the sensitivity, resolution, and medical value of modern Compton imaging. Specifically, the system will detect breast cancer lesions measuring 1 to 2 millimeters. Unlike mammography, which detects elemental composition with an 80 percent false-positive rate, our system will detect the presence of molecular signatures unique to cancer cells. This detector concept is also being developed for standoff detection of radionuclides at borders and other portals.

Major Accomplishments in 2002

We finished an advanced gamma-ray imaging systems study for both national-security and medical radioisotope detection purposes. We concluded that a semiconductor-based hybrid Compton imaging system with position-sensitive silicon and cadmium–zinc–telluride promises the highest sensitivities. In addition, we assembled a system applicable to isotopes proposed for the molecular-based detection of cancer (e.g., technetium-99m, indium-111, and iodine-131) and to new radioisotopes with potentially higher gamma-ray energies. We also acquired the first Compton camera images with a single high-purity germanium (HPGe) detector system (Figure 3).

Future Goals

We are characterizing the two-detector HPGe system to nuclear-medicine imaging specifications, assembling the first high-purity silicon (HPSi) component, and improving detector sensitivity through digital signal processing. We plan to assemble the first HPSi–HPGe hybrid Compton imager, assemble the first cadmium–zinc–telluride detectors for inclusion in a Compton imager, and further improve sensitivity through advanced image reconstruction.

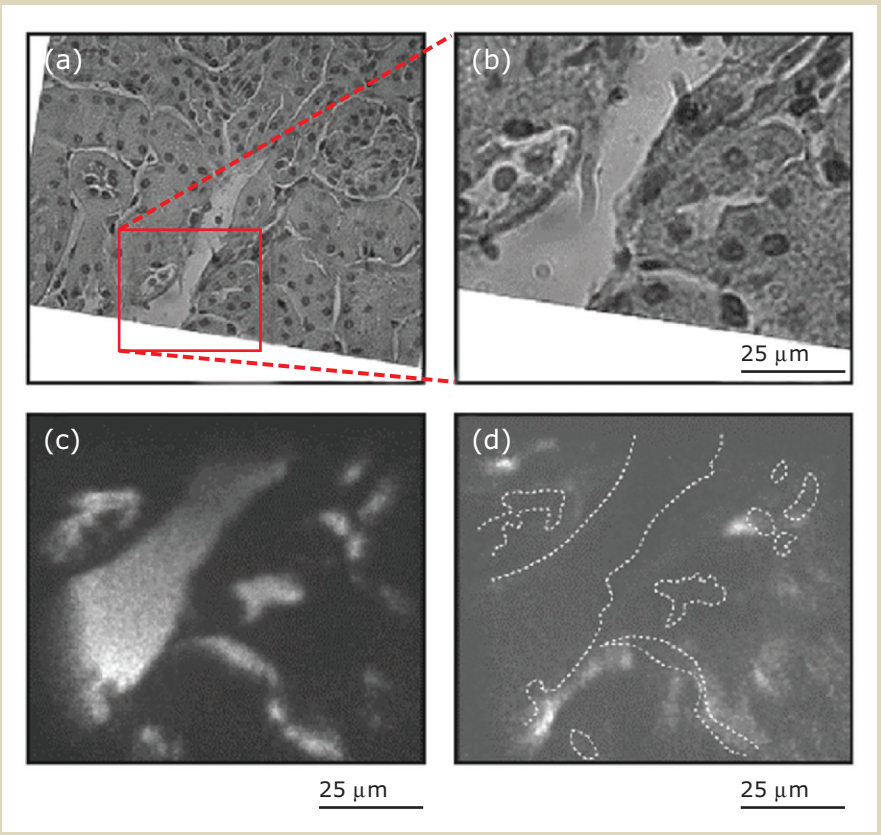

Figure 2. (a) A bright-field microscopy image at 40× magnification of a hematoxylin–eosin-stained, paraffin-embedded section of a mouse kidney cortex. (b) A region of (a) that has been enlarged as a reference for secondary ion mass spectrometry imaging in (c) and (d). (c) Potassium imaging of a 75- by 75-micrometer raster of (b). (d) Yttrium data in the raster region shown in (c). The dashed line demarcates regions of high potassium. The potassium signal is most intense in the open spaces within and surrounding the tubules and within the blood vessel, whereas the yttrium is localized within the cells surrounding those spaces.

Patient-Specific Radiation Dosimetry

A key challenge in targeted radionuclide therapy is optimizing drug administration by predetermining which patients will most benefit from therapy. Targeted radionuclide therapy has a unique feature that can be exploited for this purpose: the radioactive atoms carried by the targeting agent often emit both short-range electrons, which deliver the cytotoxic radiation-absorbed dose, and long-range gamma rays (energetic photons), which can be imaged outside the body. The result is that a diagnostic test dose of the radiolabeled drug can be used with 2- and 3-D radiation imaging to quantify the time-dependent location of the drug or radionuclide, calculate the corresponding radiation dose to tumors and organs, and ultimately estimate both tumor control and tissue complications.

The MINERVA system is being developed in collaboration with clinicians at UC Davis and researchers at Montana State University and the Idaho National Engineering and Environmental Laboratory. MINERVA focuses the LLNL-developed PEREGRINE system, the first Monte Carlo dose-calculation tool to be approved by the Food and Drug Administration for radiation therapy planning, on molecular targeted radionuclide therapy. Specifically, MINERVA calculates patient-specific radiation dose estimates by using computed tomography (CT) to describe patient anatomy in combination with a user-defined 3-D radiation source.

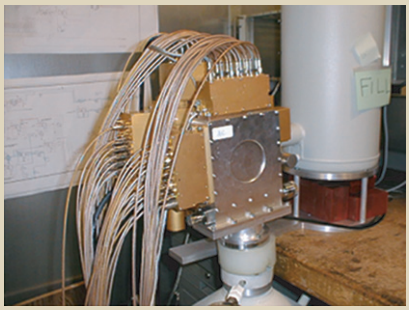

Figure 3. The first high-purity germanium detector configuration.

Major Accomplishments in 2002

We published 3-D Monte Carlo code simulations using actual patient CT scans and a validation of the PEREGRINE code system for internal radiation sources. Figure 4 shows a Monte Carlo-simulated dose for a UC Davis patient receiving molecular targeted radionuclide therapy for advanced breast cancer. We also used Monte Carlo simulations to investigate the gene expression resulting from radiation doses to conventional radiotherapy patients.

Future Goals

Our MINERVA results have led to a proposed homeland security effort in using genomic and proteomic methods for postexposure radiation dosimetry and triage of individuals exposed to nuclear and radiological weapons.

Authors

C. Hartmann Siantar, R. Balhorn, M. Colvin, M. Cosman, T. Daly, G. Denardo, M. Descalle, L. Dugan, I. Hutcheon, J. Lehmann, F. Lightstone, J. Perkins, C. Ramon, K. Vetter, and P. Weber

New Frontiers

In addition to developing targeting agents, radiation detection, and pharmacokinetics for molecular targeted radionuclide therapy, we are deepening our understanding of the very processes by which radiation causes damage in living tissues.

Together with scientists in the Biology and Biotechnology Research Program, we are initiating investigations into the genomic and proteomic response of cells following radiation exposure, with the goals of providing accurate postexposure dosimetry for nuclear and radiological weapons of mass destruction and elucidating the mechanisms that underlie the effectiveness (and side effects) of using radiation to treat cancer.

Related Publications

Descalle, M. -A. et al. Application of MINERVA Monte Carlo Simulations to Targeted Radionuclide Therapy. *Cancer Biotherapy and Radiopharmaceuticals,* **2003,** *18,* 71.

Hartmann Siantar, C. L. et al. Impact of Nodal Regression on Radiation Dose for Lymphoma Patients Following Radioimmunotherapy. *Journal of Nuclear Medicine,* in press.

Hartmann Siantar, C. L. et al. Treatment Planning for Molecular Targeted Radionuclide Therapy. *Cancer Biotherapy and Radiopharmaceuticals* **2002,** *17,* 267.

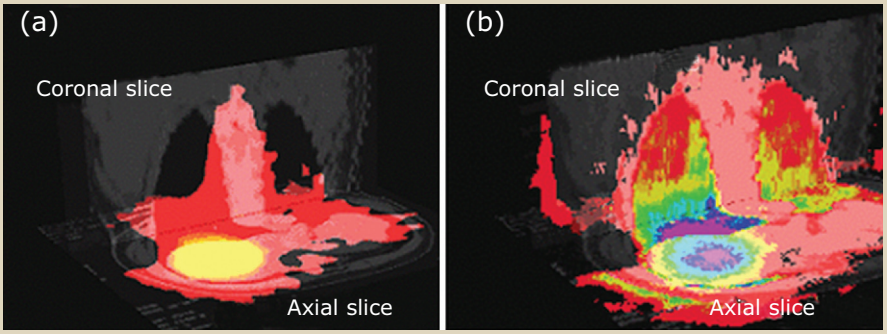

Figure 4. Coronal- and axial-slice views of (a) a fused computed tomography (CT)/single-photon-emission CT image and (b) a CT/radiation-absorbed dose image, shown for a patient with advanced breast cancer. In (a), high-to-low radioactivity is shown by yellow (high), red (low), or clear (none). In (b), the color (purple, blue, aqua, green, yellow, red, clear) indicates the radiation-absorbed dose level, from purple (high dose) to clear (no dose).

Compilation of Related Publications for the CMS Research Theme Articles

Materials Properties and Performance under Extreme Conditions

Dynamic Properties of Metals: Predictive Modeling

Bulatov, V. V.; Cai, W. Nodal Effects in Dislocation Mobility. *Physical Review Letters* **2002,** *89,* 115501.

Marian, J. et al. Dynamic Transitions in Dislocation Motion: From Smooth to Rough to Twinning. *Science*, submitted for publication, 2003.

Zbib, H. M. et al. Multiscale Model of Plasticity Based on Discrete Dislocation Dynamics. *Transactions of the American Society of Mechanical Engineers* **2002,** *74,* 78.

Impulsive Stimulated Light Scattering in the Diamond Anvil Cell

Crowhurst, J. C. Surface Waves in Germanium Single Crystals. *Applied Physical Letters*, submitted for publication, 2003.

Crowhurst, J. C. et al. Surface Acoustic Waves in the Diamond Anvil Cell: An Application of Impulsive Stimulated Light Scattering. *Physical Review B* **2001,** *64,* 100103.

Laser-Driven Shock Compression of Matter

Colvin, J. D. et al. Computational Model for a Low-Temperature Laser–Plasma Driver for Shock Processing of Metals and Comparison to Experimental Data. *Physics of Plasmas*, in press.

Colvin, J. D. et al. Spall Behavior of Laser-Shocked Sn: Comparison of Modeling to Experimental Data. *The Minerals, Metals, and Materials Society 2003 Annual Meeting Bulletin* **2003,** *55,* 293.

Nanomaterials Research: Nanoclusters, Quantum Dots, and Positrons

Nanoclusters

Bostedt, C. et al. Evidence for Cubic Phase in Deposited Germanium Nanocrystals. *Journal of Physics: Condensed Matter* **2003,** *15,* 1017.

Bostedt, C. et al. Photoemission Spectroscopy of Germanium Nanocrystal Films. *Journal of Electron Spectroscopy and Related Phenomena* **2002,** *126,* 117.

Raty, J. -Y. et al. Quantum Confinement and Fullerenelike Surface Reconstructions in Nanodiamonds. *Physical Review Letters* **2003,** *90,* 37401.

Quantum Dots and Positrons

Saniz, R. et al. Compton Scattering, Positron Annihilation, and the Electronic Properties of Quantum Dots. *Physical Review B* **2002,** *65,* 245310.

Weber, M. et al. Direct Observation of Energy-Gap Scaling Law in CdSe Quantum Dots with Positrons. *Physical Review B* **2002,** *66,* 41305.

Recent Advances in Plutonium Science

Fluss, M. J. et al. Temperature-Dependent Defect Properties from Ion Irradiation in Pu(Ga). *Journal of Alloys and Compounds*, submitted for publication, 2003.

Nelson, E. J. et al. Local Structure and Vibrational Properties of α′-Pu Martensite in Ga-Stabilized δ-Pu. *Physical Review B*, submitted for publication, 2003.

Schwartz, A. J. et al. Characterization and Modeling of Helium Bubbles in Self-Irradiated Plutonium Alloys. *Philosophical Magazine,* submitted for publication, 2003.

Strain-Rate Scaling of Deformation Mechanisms

Edwards, J. et al. A Laser-Driven Plasma Loader for Shockless Compression and Acceleration of Samples in the Solid State. *Physical Review Letters*, submitted for publication, 2003.

McNaney, J. M. et al. High Pressure, Laser-Driven Deformation of an Aluminum Alloy. *Metallurgical Transactions A*, submitted for publication, 2003.

Remington, B. A. et al. TMS Annual Paper. *Metallurgical Transactions*, submitted for publication, 2003.

Chemistry under Extreme Conditions and Chemical Engineering in Support of National-Security Programs

Advanced Sol-Gel Synthesis

Gash, A. E. et al. New Sol-Gel Synthetic Route to Transition and Main-Group Metal Oxide Aerogels Using Inorganic Salt Precursors. *Journal of Non-Crystalline Solids* **2001,** *285,* 22.

Gash, A. E. et al. Use of Epoxides in the Sol-Gel Synthesis of Porous Iron(III) Oxide Monoliths from Fe(III) Salts. *Chemistry of Materials* **2001,** *13,* 999.

Tillotson, T. M. et al. Nanostructured Energetic Materials Using Sol-Gel Methodologies. *Journal of Non-Crystalline Solids* **2001,** *285,* 338.

Aromaticity Provides Bucky Stability in Aza-Fullerenes

Aromaticity Provides Bucky Stability. *Chemical & Engineering News* **2002,** *80,* 30.

Manaa, M. R. et al. High-Energy Structures of Azafullerene $C_{48}N_{12}$. *Chemical Physics Letters*, submitted for publication.

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Quantum Molecular Vibrations: A New Frontier in Computational Chemistry

Glaesemann, K. R.; Fried, L. E. Improved Heat Capacity Estimator for Path Integral Simulations. *Journal of Chemical Physics* **2002,** *117,* 3020.

Glaesemann, K. R.; Fried, L. E. An Improved Thermodynamic Energy Estimator for Path Integral Simulations. *Journal of Chemical Physics* **2002,** *116,* 5951.

Glaesemann, K. R.; Fried, L. E. A Path Integral Approach to Molecular Thermochemistry. *Journal of Chemical Physics* **2003,** *118,* 1596.

Understanding Energetic-Material Response

Gee, R. H.; Fried, L. E. Ultrafast Crystallization of Polar Polymer Melts. *Journal of Chemical Physics* **2003,** *118,* 3827.

Maienschein, J. L. et al. Understanding and Predicting the Thermal Explosion Violence of HMX-Based and RDX-Based Explosives: Experimental Measurements of Material Properties and Reaction Violence. *Proceedings of the 12th International Detonation Symposium,* San Diego, CA, August 11–16, 2002. Office of Naval Research, in press.

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Science in Support of National Objectives at the Intersection of Chemistry, Materials Science, and Biology

Multiscale Computational Chemistry: Modeling of Aerosol and Combustion Chemistry

Gee, R. H.; Fried, L. E. Ultrafast Crystallization of Polar Polymer Melts. *Journal of Chemical Physics* **2003,** *118,* 3827.

Mundy, C. J. et al. Irradiated Guanine: A Car-Parinello Molecular Dynamics Study of Dehydrogenation in the Presence of an OH Radical. *Journal of Physical Chemistry* **2002,** *106,* 10063.

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Westbrook, C. K. et al. A Detailed Chemical Kinetic Modeling Study of the Shock Tube Ignition of Isomers of Heptane. *International Journal of Chemical Kinetics* **2001,** *33,* 868.

Scanning Probe Nanolithography for Controlled Protein Deposition

Cheung, C. L. et al. Fabrication of Assembled Virus Nanostructures with Chemoselective Linkers by Scanning Probe Nanolithography. *Journal of the American Chemical Society,* in press.

Noy, A. et al. Fabrication of Luminescent Nanostructures and Polymer Nanowires Using Dip-Pen Nanolithography. *Nano Letters* **2002,** *2,* 109.

Weeks, B. L. et al. Effect of Dissolution Kinetics on Feature Size in Dip-Pen Nanolithography. *Physical Review Letters* **2002,** *88,* 5505.

Single-Cell Proteomics with Ultrahigh-Sensitivity Mass Spectrometry

Fergenson, D. P. et al. Instantaneous Reagentless Identification of Individual Bioaerosol Particles. *Nature*, in press.

Steele, P. T. et al. Laser Power Dependence of Mass Signatures from Individual Bacterial Spores in Bioaerosol Mass Spectrometry. *Analytical Chemistry*, in press.

Applied Nuclear Science for Human Health and National Security

Heavy Element Discoveries: Elements 114 and 116

Oganessian, Y. T. et al. Observation of the Decay of (292)116. *Physical Review C* **2000,** *63,* 1301.

Oganessian, Y. T. et al. Synthesis of Superheavy Nuclei in the $^{48}Ca + ^{244}Pu$ Reaction: (288)114. *Physical Review C* **2000,** *62,* 1604.

Oganessian, Y. T. et al. Synthesis of Superheavy Nuclei in the Reactions of Pu-244 and Cm-248 with Ca-48. *European Physical Journal A* **2002,** *15,* 201.

The Bionuclear Research Initiative: Molecular Targeted Radionuclide Therapy

DeNardo, G. L. et al. Impact of Interpatient Pharmacokinetic Variability on Design Considerations for Therapy with Radiolabeled Mabs. *Cancer Biotherapy and Radiopharmaceuticals,* in press.

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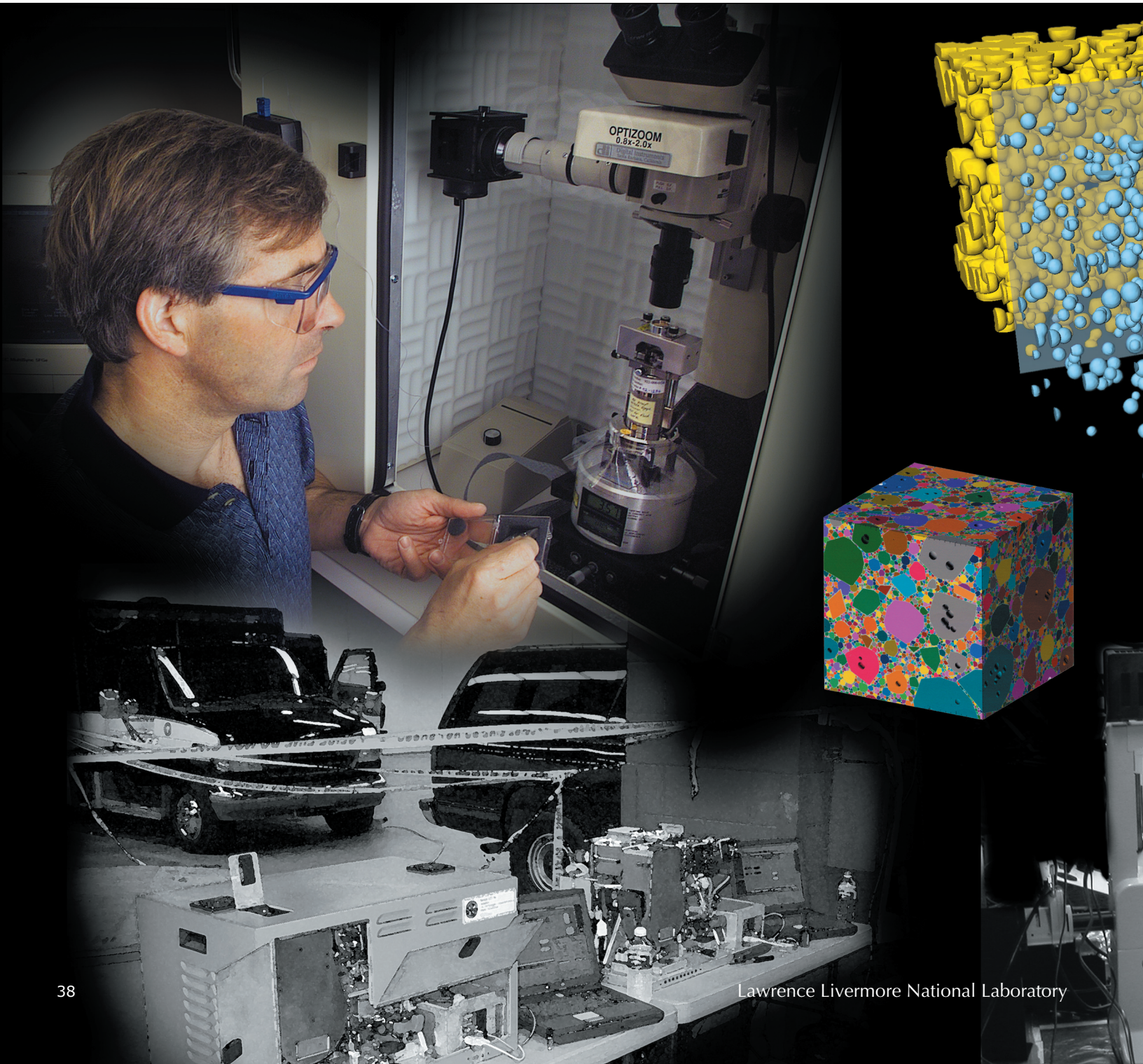
Hartmann Siantar, C. L. et al. Impact of Nodal Regression on Radiation Dose for Lymphoma Patients Following Radioimmunotherapy. *Journal of Nuclear Medicine,* in press.

Hartmann Siantar, C. L. et al. Treatment Planning for Molecular Targeted Radionuclide Therapy. *Cancer Biotherapy and Radiopharmaceuticals* **2002,** *17,* 267.

Dynamic Teams...



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Divisions
Centers
Institutes

Analytical and Nuclear Chemistry Division

The Analytical and Nuclear Chemistry Division (ANCD) staff seeks to position the division at the intersection of the chemical, biological, and nuclear sciences and to provide unique and combined solutions with a strong focus on national security. The core strength of ANCD scientists is their ability to cross disciplinary boundaries, organize, and work collaboratively to meet new institutional challenges (Figure 1). ANCD has also focused on reinforcing affiliations with the Laboratory's Nonproliferation, Arms Control, and International Security (NAI) programs. Historically, the division's strengths have been in radiochemistry, radiation detection and spectroscopy, mass spectrometry, and analytical chemistry. These strengths have been augmented to include biochemistry with an emphasis on modeling and analytical science.

In addition to performing applied research in support of Laboratory programs, ANCD scientists pursue fundamental research in several areas, including plutonium science, heavy-element research, noncovalent interactions among biomolecules, transport of actinide colloidal complexes in groundwater, cycling of iodine in the environment, and isotopically enhanced molecular targeting.

For example, the heavy-element research group, in collaboration with scientists at the Joint Institute for Nuclear Research in Dubna, Russia, recently published the discovery of new superheavy elements. In 2000, they reported the synthesis of element 116; in 2002, they focused on research to determine the chemical properties of these novel elements.

Theme-Related Accomplishments in 2002

Science in support of national objectives at the intersection of chemistry, biology, and materials science:

- Partnered with the Defense Threat Reduction Agency to develop capabilities to respond to potential acts of domestic nuclear terrorism.
- Participated in analytical trials leading to Lawrence Livermore's laboratory certification by the Organization for the Prohibition of Chemical Weapons in the Hague.
- Partnered with the National Ignition Facility (NIF) team to accomplish first light to the target chamber.
- Expanded the BioSecurity and Nanosciences Laboratory's scientific base and studies to defend against biological threats to human health and the environment.
- Developed programs in the areas of consequence management and nuclear attributions to support the new Department of Homeland Security.
- Led a program to design and deploy radiation detectors to identify potential nuclear materials at major U.S. ports of entry.

Applied nuclear science for human health and national security:

- Continued support to the stockpile stewardship program by reducing uncertainties associated with the historical nuclear test data that are required to accurately model the performance of nuclear weapons in the absence of underground nuclear testing.
- Pursued studies of plutonium metal and materials compatibility and aging to extend the life cycle of U.S. nuclear weapons in the current stockpile.
- Investigated the mobility of radionuclides at sites throughout the country contaminated by Cold War atomic defense production and testing.
- Collaborated with governments in the former Soviet Union, the Middle East, and the Persian Gulf to address environmental threats in these regions and to promote regional security.

- Led a program with the Environmental Protection Department to determine the susceptibility to volatile organic contamination of more than 15,000 public water supply wells throughout the state of California using measurements of water quality and age.

- Expanded the client base of the Chemical Environmental Services Laboratory to include the non-standard sample analyses required to decommission and dismantle surplus buildings and radiochemical facilities at Lawrence Livermore.

Facility Highlights

ANCD facilities continued to be enhanced and expanded in 2002. One example is the construction of a two-story, general-purpose office building adjacent to the radiochemistry building. When completed in mid-2003, the office building will house a classified data center on the second floor, as well as unclassified general-office space, an administrative suite, and a large auditorium with state-of-the-art presentation equipment on the first floor.

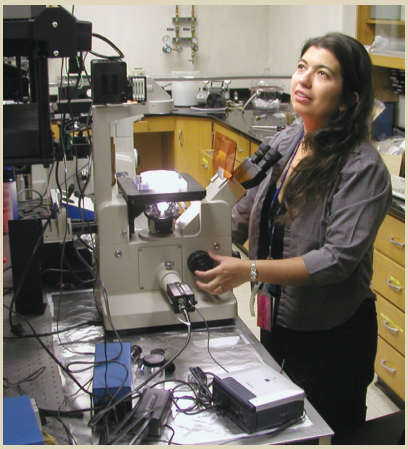

Figure 1. Adding a significant number of younger scientists has invigorated and expanded ANCD's scientific capabilities, which are now coupled to all major Laboratory programs.

State-of-the-Art Technologies

Using a diverse analytical base, ANCD scientists conduct measurements for a wide variety of Laboratory programs. Over the past several years, ANCD has invested in state-of-the art instrumentation that positions the division as a leader in analytical science.

In 2002, our IsoProbe magnetic sector inductively coupled plasma spectrometer was used to analyze plutonium and uranium isotope ratios for national-security programs with accuracy and at extremely high precision. This multiprogram facility supports the International Atomic Energy Agency, the Stockpile Stewardship Program, and others that require ultratrace element analysis.

Our bioaerosol mass spectrometer facility allows for the rapid discrimination of micrometer-scale single cells and spores in complex backgrounds. This capability allows harmful airborne spores to be differentiated instantaneously from benign cells. Methods employing matrix-assisted laser desorption ionization and Fourier transform ion cyclotron resonance mass spectrometry are rapidly becoming the capabilities of choice for studies related to the cell life cycle, protein mapping, and pre-symptomatic disease detection.

The Center for National Security Applications of Magnetic Resonance, which was established in 2002, includes 300-, 400-, and 600-MHz spectrometers with solid- and liquid-state probes to provide non-destructive analysis of chemical speciation, chemical structure, and chemical dynamics. These data are important to basic research as well as to applied programs such as stockpile stewardship and bioscience.

ANCD's new secondary ionization mass spectrometer, the NanoSIMS, will provide unprecedented analytical sensitivity, high spatial resolution (up to 50 nanometers) and multi-isotope imaging. The NanoSIMS will allow isotopic and elemental studies at the subcellular scale for biological studies, as well as high-resolution material composition and structure studies important to national-security programs (e.g., element distribution in alloys, failure analysis, and nuclear forensic investigations). This instrument will become fully operational in 2003.

Future Goals

We have identified three science-and-technology thrust areas to support the CMS Directorate's strategic plan: science at the intersection of chemistry, biology, and materials science; applied nuclear science; and environmental science. To better align the division's scientific capabilities to the Laboratory's strategic mission, ANCD has been reorganized along three guiding themes centered on nuclear science, chemical science, and bioanalytical science. This new structure will allow division scientists to better meet programmatic commitments and optimally develop relevant supporting scientific capabilities.

With continued growth expected in ANCD in 2003, we are appropriately positioned to meet programmatic commitments and define the fundamental science required for the future success of the Laboratory's major programs. In addition, the activities described in the Theme-Relevant Accomplishments in 2002 section will continue to be a central focus for ANCD in the years to come. We are optimistic about the future of our division and our ability to make significant contributions to the success of primary missions throughout the CMS Directorate and the Laboratory.

Author
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Chemistry and Chemical Engineering Division

The Chemistry and Chemical Engineering Division (CChED) has a primary goal of supporting the major Laboratory missions. To accomplish this while being recognized by the scientific community at large, the division is organized into nine program elements and scientific capabilities: energetic materials; weapon materials compatibility and aging; National Ignition Facility (NIF) optics; NIF target fabrication; NIF materials; Nonproliferation, Arms Control, and International Security (NAI); extreme chemistry; computational chemical biology; and advanced material synthesis. Each area has a leader who is responsible for growth and development in both the programmatic and technical areas.

Theme-Related Accomplishments in 2002

CChED is aligned with the CMS research theme of *chemistry under extreme conditions and chemical engineering in support of national-security programs*. The following are highlights of CChED accomplishments:

- Using a new energetic molecule (LLM-105), we developed a prototype for an insensitive high-explosives booster.

- Our chemical engineers and physical chemists who are matrixed to NIF led efforts in optical materials development, optics fabrication, and optical assembly. This work culminated in the completion of the main laser beampath for the first four beamlines on NIF.

- CChED personnel were part of a team that achieved a significant accomplishment in Advanced Simulation and Computing (ASCI) material modeling by reaching the Level 2 Milepost on Grain-Scale Dynamics in Explosives on September 30, 2002. This milepost required the team to develop a model for the detonation process in high explosives based on chemical and physical processes that occur on the grain scale (submicrometer). Developing the model involved a combination of experimental work (e.g., deflagration behavior), computational activities (e.g., adding physics modules to the ALE3D code), and model development (e.g., hot-spot ignition and flame spread). This work culminated in a science-based model of detonation that was successfully applied to numerically simulate existing detonation data.

- Our computational chemists used electronic-structure techniques to propose a novel energetic material consisting of a nitrogen analog (N_{60}) of the carbon buckyball. Although only metastable, this compound would provide enormous energy-storage capabilities. In addition, continued development of computational tools to model the reactive flow in energetic materials led to a new edition of the internationally used CHEETAH code.

- We also helped develop a new glucose sensor for use in miniaturized, implanted diagnostic and treatment methodologies. This work, performed under a cooperative research and development agreement with MiniMed, Inc., received a Department of Energy Bright Light Award and a Federal Laboratory Consortium Award.

Facility Highlights

The Energetic Materials Center (EMC) is a collection of world-class experimental facilities and theoretical and computational capabilities—a unique cornerstone of CChED. The range of facilities and experimental activities at EMC enables work investigating quantities from less than 1 gram to greater than 100 kilograms.

State-of-the-Art Technologies

The Energetic Materials Program Element's activities cover a wide range of basic research and programmatic activities in support of stockpile stewardship, conventional defense, and other national needs. Researchers combine breakthrough computer simulation codes; state-of-the-art experimental diagnostics; and a culture in which theoretical, synthesis, and experimental chemists

and physicists work alongside one another. These teams synthesize new insensitive high explosives with properties tailored to the needs of weapon designers, scale up manufacturing processes to make large amounts of energetic materials for testing and evaluation, characterize energetic materials with regard to their safety and performance, and develop and use computer models that simulate microscale to full-scale conditions.

Computational chemistry is a central part of our research portfolio. For example, reaction mechanisms have been developed to study the influence of fuel molecular structure on ignition properties, such as the octane and cetane ratings of automotive fuels. In addition, research in the computational chemistry of heavy elements uses relativistic electronic-structure techniques to study actinide-element chemistry. Moreover, in chemical-warfare (CW) agent modeling, kinetic models for surrogate and actual CW agent chemicals are being developed for use in a variety of scenarios (e.g., atmospheric dispersion, accidents, and terrorist events). Finally, work in the computational chemistry of energetic materials investigates the detonation and slow combustion of explosives, the kinetics of high-energy density materials, and the electronic-structure modeling of high explosives.

Chemical synthesis and processing efforts produce novel materials for a wide range of programmatic efforts. The most highly developed capability, sol-gel and aerogel research and technology, has been used for several years to produce coating materials for NIF optics and ultralow-density materials for Defense and Nuclear Technologies (DNT) and other programs. An important new development has generalized the synthesis technique for low-density materials so that aerogels and other ultralow-density materials can be synthesized by incorporating almost every element in the periodic table. This marked improvement over previous sol-gel methods increases the flexibility and variety of applications of such materials.

Our chemical engineers are involved in a number of high-profile projects; many of these engineers hold key leadership positions. For example, our chemical engineers are major participants in NAI programs, such as the Counterproliferation Analysis and Planning System, where they conduct foreign-threat assessments of the capabilities for developing weapons of mass destruction. In support of NIF Programs, our chemical engineers are also developing techniques to mitigate etch pitting on optical surfaces, reduce defects in optics resulting from manufacturing and processing, and significantly improve the production of diffractive optics (Figure 1). Recent chemical-engineering contributions in the area of energetic materials include the development of new alternative methods for destroying unstable and excess munitions. This research has resulted in the commissioning and licensing of a new type of molten-salt unit for destroying waste high explosives for the U.S. Army.

Author
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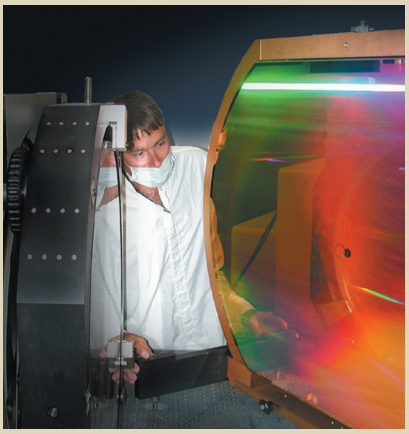

Figure 1. A 94-centimeter-diameter diffraction grating produced by the Diffractive Optics Group in the Chemistry and Chemical Engineering Division.

Future Goals

Our main goal is to enhance our capabilities in the area of chemistry and chemical engineering under extreme conditions. There is a core need in many Laboratory programs to understand dynamic chemical processes at high temperatures and very high pressures in the condensed fluid phase. Examples include high explosives, verified in situ destruction of chemical or biological weapons of mass destruction, and the possible origins of life on Earth from the interstellar delivery of organic molecules. In these examples, there are fundamental questions that remain unanswered: What happens at short time scales? How and when do molecules dissociate in a shock process?

Answers to these questions may pave the way to understanding how the reaction products of explosives are formed or how simple interstellar organic molecules can polymerize in a cometary impact. Although equilibrium (thermodynamic, chemical, and ionization) is often assumed in shock experiments based on the rapid collision rates in condensed systems at high pressures and temperatures, no experiments have been performed to determine how and when equilibrium is achieved. In fact, whether our conventional chemical notions still hold at extreme conditions is unclear. Our new initiative in extreme chemistry, in collaboration with Physics and Advanced Technologies and DNT, should provide answers to many of these questions.

CChED will continue to support the NIF Programs Directorate by guiding the development of novel and improved optical materials and optics fabrication processes to ensure the success of the NIF construction project and to enable NIF's varied scientific missions. Efforts in small-tool and wet-etch figuring will provide diffractive optics for NIF and other large-aperture, solid-state lasers around the world.

Materials Science and Technology Division

The Materials Science and Technology Division (MSTD) is organized into a number of program elements and scientific capabilities. The three main programmatic business units in MSTD are stockpile science, including low- and high-energy-density materials science; homeland security; and energy and environment. Program elements are aligned with specific projects in the Defense and Nuclear Technologies; National Ignition Facility (NIF); Nonproliferation, Arms Control, and International Security (NAI); and Energy and Environment directorates.

In addition to the core scientific competencies in MSTD, the division supports cross-cutting scientific capabilities in ultrascale computational materials science, materials synthesis, and nanobeam precision characterization.

Figure 1. The transmission electron microscope in the Materials Science and Technology Division enables scientists to better observe, model, and predict plutonium's long-term behavior.

Theme-Related Accomplishments in 2002

The following MSTD accomplishments are aligned with the CMS research theme of *materials properties and performance under extreme conditions:*

- Determination of the full-zone phonon dispersion curves in plutonium on the basis of inelastic x-ray scattering.
- Design and fielding of experiments on laser-driven shock and shockless compression of tantalum at high strain rates.
- Ultrascale molecular dynamics simulations of shock compression in copper, revealing the transition from a uniaxial to a quasi-hydrostatic stress state.
- Synthesis and characterization of nanograin crystalline copper for optimized materials performance.
- Spatially resolved structural characterization of complex physical and chemical phases of plutonium using electron energy loss spectroscopy

within a transmission electron microscope (TEM).

- Continued support of the Yucca Mountain Project.

Facility Highlights

Important infrastructure enhancements were added to the MSTD materials-characterization capability in 2002. A time-of-flight secondary ion mass spectrometer and a new electron spectroscopy for chemical analysis system were acquired, installed, and activated. Existing surface-science laboratory space was consolidated to make room for the new instrumentation. MSTD is currently in the process of adding a second Type III radiological workplace to Building 235 to increase the throughput of the plutonium sample preparation area. Finally, a new plutonium science laboratory was constructed to perform small-scale experiments on encapsulated samples.

Significant progress was also made on the cleanup of legacy materials in Building 241, thereby eliminating a large burden of unusable space. The reclaimed space has already been reused, enabling NAI's Biological Aerosol Sentry and Information System Program to rapidly deploy over 7000 square feet of new offices and laboratories.

State-of-the-Art Technologies

MSTD has developed a unique laboratory for preparing plutonium specimens for transmission electron microscopy. Using this facility, plutonium specimens were examined in the TEM (Figure 1), and their aging microstructures were characterized at a near-atomic level of resolution. In addition, the state-of-the-art TEM has been adapted to perform in situ analytical measurements on dynamically strained specimens.

Recent accomplishments of the materials-characterization capabilities include detailed materials investigations for NIF laser optics. A precision ultrahigh-vacuum bonding facility enables MSTD scientists to investigate tailored interfaces between a wide range of materials. These capabilities support the dual missions of fundamental materials research and direct support of Laboratory programs. Specific examples of signature science afforded by these capabilities can be found in the nanoscience and technology areas of crystal growth, quantum confinement, and biological–inorganic interfaces.

MSTD maintains expertise in characterizing and modeling the mechanical properties of metals and in developing the relationships between microstructure and properties. This expertise also includes experience with the mechanical properties of inorganic composite materials. The joining element spans the entire range of metallic and nonmetallic inorganic materials joining, with a specialty in the joining of exotic, toxic, or hazardous materials.

The ceramics capability is focused primarily on fabricating monolithic parts from ceramic powders using hot pressing, sintering, hot isostatic pressing, or plasma spraying techniques. MSTD also maintains a well-equipped metallography laboratory to serve the needs of many programs.

MSTD has established a world-class, high-performance materials modeling and simulation capability to predict materials properties and response over many length scales, from quantum-mechanical to continuum descriptions.

Representative activities include first-principles calculations of fundamental (electronic, thermodynamic, optical, magnetic, and transport) properties of materials; ultrascale atomistic simulations applied to defects and diffusion in solids (e.g., radiation damage and ion implantation); shock compression of materials; laser–materials interactions; microscale simulations of dislocation structure evolution in materials undergoing external strain; and mesoscale modeling of processes (e.g., metalworking operations such as casting, welding, dynamic fracture and failure, and void growth).

The division's materials theory, modeling, and simulation core capabilities are essential tools to enable the Laboratory's current and future missions and to provide engines of scientific discovery.

Future Goals

MSTD's goal is to establish uncontested leadership in the emerging field of high-energy-density materials science by developing a vigorous, integrated, and comprehensive program to investigate the properties and performance of materials subjected to extreme dynamic conditions of pressure, temperature, strain, and strain rates. A particular focus will be the design of extreme dynamic materials experiments and the development of advanced in situ, real-time diagnostics on NIF and other high-energy-density experimental platforms.

Establishing a Target Science and Nanoscience Laboratory (TSNL) will enable MSTD scientists to link and integrate programmatic requirements with materials synthesis and assembly. Consequently, the role of TSNL will be to incubate research-and-development activities leading to next-generation target science for weapons and inertial confinement fusion applications.

Author
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Dynamic Teams:
A center that conducts scientific research to protect the nation against biological threats and natural-disease outbreaks

BioSecurity and Nanosciences Laboratory

The BioSecurity and Nanosciences Laboratory (BSNL) is a multidisciplinary, multiprogrammatic initiative among five major directorates at Livermore:

- Biology and Biotechnology Research Program
- Chemistry and Materials Science
- Energy and Environment
- Nonproliferation, Arms Control, and International Security
- Physics and Advanced Technologies

BSNL's technical mission is to detect, identify, and characterize harmful molecules such as viruses, spores, bacteria, and chemical toxins. Principal research areas at BSNL include proteomic analysis, bioaerosol science, biological signatures, and the study of biochemical systems and biomolecular function. A fifth major area of research is the development of pathogen and toxin detection methods that are not based on polymerase chain reaction (PCR).

CMS Research Theme Alignment

In alignment with the CMS research theme of *science in support of national objectives at the intersection of chemistry, materials science, and biology*, BSNL scientists conduct multidisciplinary research that helps our nation fight biological weapons and life-threatening diseases. Our research findings can be used to help the nation's homeland security organization counter bioterrorism and to improve human health.

Major Accomplishments in 2002

Sophisticated computer modeling underlies most BSNL research activities by providing the framework to both design and understand experiments. During 2002, we broadened our expertise in predicting the fate of bioaerosols through terascale computing and in simulating signaling pathways in epithelial cells.

Bioaerosol mass spectrometry (BAMS) is being used to detect single bacterial spores, viruses, and toxins in real time. This analytical capability offers the possibility of identifying and quantifying selected cell types

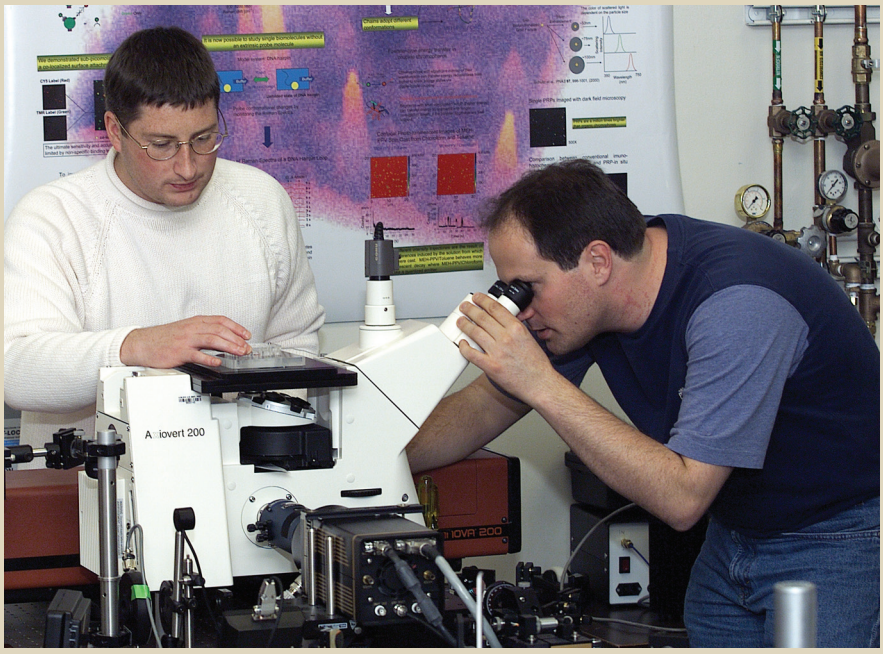

Figure 1. BSNL scientists are developing optical microscope methods for signaling the presence of individual toxin molecules. Such methods would enable the eventual detection of ultralow concentrations of harmful substances (e.g., viruses or bacteria).

within a complex background containing multiple cellular, biochemical, and nonbiological components. BAMS also provides a method for analyzing the chemical evolution of individual organisms that have been sampled from a broader population.

BSNL scientists are developing carbon nanotube arrays in microfluidic devices to serve as biosensors. A carbon nanotube can act as a molecular wire with a conductivity greater than copper. Because carbon nanotubes are almost weight-free, take up little space, and have an enormous surface-to-volume ratio, they have a high collection efficiency, making them ideal for collecting biological and chemical agents.

In another area of active research, BSNL scientists are developing optical microscopy methods to signal the presence of individual toxin molecules (Figure 1). Such methods would enable the detection of ultralow concentrations of harmful substances (e.g., DNA, viruses, or bacteria) and of protein markers for diseases. Other biodetection efforts are using smart membranes, pores in silicon that are chemically treated to capture target biomolecules, and microcantilevers, thin bars of silicon nitride that bend when target biomolecules attach to the silicon nitride surfaces. To make these detection technologies viable, BSNL is investing in methods to synthesize reactive compounds that have been designed to bind strongly to specific biomolecules and that can, in turn, be attached to the surfaces of biodetectors.

The Fourier transform mass spectrometer (FTMS) can help bioterrorist hunters and medical researchers find presymptomatic disease biomarkers. By using FTMS to examine molecules in a cell, scientists can determine if the cell is in the early stages of a disease (e.g., anthrax, smallpox, plague, or cancer). In 2002, we coupled nanobore liquid chromatography, a method for separating individual protein markers, to FTMS to enable the analysis of complex protein mixtures.

In addition, BSNL scientists are developing methods for finding the biological signatures of spores, viruses, and bacteria. These methods are based on advanced physical and chemical characterization tools, such as atomic force microscopy and ion microprobe analysis of single organisms. These tools also provide a means for correlating the evolution of the physical and chemical structure of organisms with environmental conditions and the genomic sequence.

State-of-the-Art Technologies

BSNL has brought together a unique suite of analytical tools that provide state-of-the-art characterization capabilities at the molecular-to-single-organism level. Our investment in optical systems with single-molecule detection capabilities supports both ultrasensitive-detection development and research into protein–protein interactions. We have also acquired the most precise mass spectrometry systems available, thereby providing a technical basis for high-throughput protein analysis and profiling of chemical signatures across individual cells.

In addition, BSNL has created atomic force microscopy laboratories with the capability to spatially resolve a structure at the single-protein level, measure interaction forces at the single-molecule level, and chemically pattern surfaces at 10-nanometer length scales. These laboratories have enabled BSNL scientists to pursue a wide range of research activities focused on both biosecurity technologies and fundamental biosciences.

Author
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Future Goals

We plan advancements in all five major research areas at BSNL. The establishment of a new bioaerosol sciences laboratory will integrate our current microscopic simulation capabilities and single-organism detection technologies with the capacity to perform microscopic measurements of bioaerosol interactions and mesoscopic measurements of bioaerosol transport and chemical and morphological evolution. In addition, new approaches to developing molecular-recognition chemistry will enable the rapid production of a large number of high-affinity binders, thereby strongly impacting our future ability to field effective non-PCR-based sensors.

In the coming years, integrating the many methods for obtaining biological signatures at the single-spore level will lead to a new level of understanding about the process of cell differentiation. In addition, combining these methods with image-extraction software will provide a useful database for biological attribution.

We also intend to use high-resolution mass spectrometry and nanobore liquid chromatography to analyze human samples. Applying these two techniques will provide a critical element in the Laboratory's effort to map human reaction to pathogenesis, whether natural or synthetic.

Finally, BSNL scientists will continue to apply their tools and expertise to fundamental issues in biochemistry and biophysics, such as determining the mechanism by which proteins direct tissue mineralization or understanding the kinetics of protein aggregation associated with prion-based diseases.

Dynamic Teams:
A center that is a national resource for the research and development of explosives, pyrotechnics, and propellants

Energetic Materials Center

Livermore's involvement in energetic materials began in 1952 when the Laboratory instituted a research and development program in high explosives for nuclear weapons. Today this work continues under the aegis of the Energetic Materials Center (EMC) as a core element of the Stockpile Stewardship Program, the centerpiece of the Laboratory's national-security mission. In addition, the scope of work has been broadened to support the research and development of energetic materials for advanced conventional weapons, rocket and gun propellants, homeland security, demilitarization, and industrial applications.

Underlying our activities in the EMC is a foundation of world-class science. The requirements of stockpile stewardship and the challenges of advanced-conventional-weapons development demand that we understand the performance of high explosives and how this may change over time. In addition, the evolving threats to homeland security have expanded the needed scope of materials knowledge. Through the EMC, Laboratory scientists and engineers are coupling measurements using modern experimental tools with advanced theoretical and computational techniques to elucidate a detailed understanding of energetic materials. They are then applying this knowledge to practical problems of national defense.

CMS Research Theme Alignment

Energetic materials release chemical energy with enormous power through extremely fast chemical reactions. Explosives are designed to detonate (i.e., react at supersonic velocity at temperatures of several thousand degrees and at pressures measuring hundreds of thousands of atmospheres). Propellants and pyrotechnics are designed to react by deflagration (i.e., very rapid combustion at temperatures of several thousand degrees and at pressures measuring hundreds of atmospheres). Under some conditions, explosives react by deflagration, and in a few cases, the deflagration may turn into a detonation. Thus, energetic materials epitomize the CMS research theme of *chemistry under extreme conditions and chemical engineering in support of national-security programs.*

Major Accomplishments in 2002

We developed a simulation of the shock initiation and detonation of a stockpile high explosive (LX-04). In contrast to previous empirical calculations, the simulation is based on the underlying physics and chemistry of the detonation. The interactions between defects and explosive grains under shock lead to detonation, and an accurate description of these interactions on the micrometer and submicrometer scale is the basis for our new simulation. This capability is particularly important for nonideal explosives, such as the insensitive high explosives used in modern nuclear weapons.

While simulating this process, we made many scientific advances. For example, we developed a model to

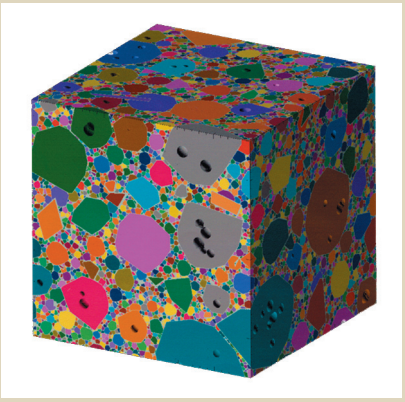

Figure 1. A computational representation of a 300-micrometer cube of LX-04. Each explosive grain is shown as a colored shape, with the binder marked in gray and defects shown as holes. This simulation contains 93,000 crystals defined by 10 million planes and 200 million zones.

describe the shock formation of hot spots and their evolution into detonation. We also developed complex computational methods to carry out reactive and hydrodynamic calculations. Figure 1 shows our representation of LX-04—a significant computational achievement in itself—featuring individual grains, the binder between grains, and the voids where hot spots can start. Figure 2 provides a snapshot of a shock as it progresses through LX-04. We measured the explosive's deflagration behavior by using a diamond anvil cell to create the detonation pressures and temperatures necessary to accurately simulate hot-spot growth. The knowledge that we gained from the LX-04 simulations enabled us to develop an improved global model for shock initiation based on physical processes. However, simulating an entire weapon-scale system on the grain scale is not yet possible because of the prohibitive computational demands.

State-of-the-Art Technologies

To understand and control the chemistry of explosive reactions (nanosecond reactions that drive microsecond detonation processes), our researchers require state-of-the-art experimental facilities. The Laboratory's unique experimental facilities include the High Explosives Application Facility (HEAF) and the Site 300 CMS facilities, in which explosives synthesis, formulation, characterization, and processing are conducted; HEAF, the Contained Firing Facility, and the Big Explosives Experimental Facility, in which fully diagnosed explosives detonations are conducted; and the Forensic Science Center, in which explosive-detection methods are developed.

We apply high-fidelity, high-speed diagnostics to dynamic experiments whenever possible, including flash radiography, high-speed streak and framing photography, laser velocimetry, and embedded pressure and particle-velocity gauges. The coupling of experimental results with new computer codes (e.g., ALE3D) and computational chemistry advances (e.g., first-principles quantum-mechanical calculations of kinetics in the picosecond time frame and path-integral Monte Carlo calculations of thermochemical properties) gives EMC researchers a unique ability to apply the latest scientific developments to the challenges posed by energetic materials.

Author
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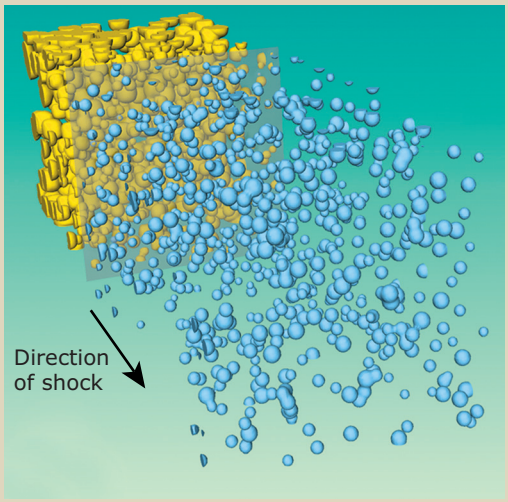


Figure 2. A snapshot from a grain-scale simulation of a shock traveling through LX-04. The shock wave (translucent plane) is traveling into an unreacted LX-04 explosive. Blue spheres in front of the shock surround the holes in the explosive. The high-pressure flame front (yellow) progresses away from each collapsed void. The hot gas created by the flame increases the pressure, thereby accelerating the shock into a detonation.

Future Goals

Our recent accomplishments highlight the approach that will be continued in our future research—a combination of cutting-edge model development and computational analysis with highly diagnosed experiments to provide scientifically based advances. Our research activities are focused in four categories: performance, safety, reliability and surveillance, and new materials.

For performance (i.e., the detonation behavior of explosives), our approach will improve our performance analysis of existing and new systems and will help develop more effective applications of explosives in the stockpile and in conventional weapons. Similarly, in safety studies (i.e., the response of energetic materials to unintended stimuli), this approach will enable us to evaluate the response of energetic materials to a wide variety of stimuli, providing a scientific basis for resolving safety questions and improving designs with respect to safety.

For reliability and surveillance questions, we will focus on a detailed understanding of aging effects in energetic materials, with the goals of identifying potential age-related changes and of extending the projected lifetime of energetic materials on a scientific basis. Finally, our efforts in new materials will be aimed at developing novel energetic molecules, formulations, and nanoenergetics to support improved safety and performance in the stockpile, as well as the national-security trend toward small, high-value weapon systems that require innovative materials.

Dynamic Teams:

A center that provides exceptional chemical and forensic analysis capabilities to support national-security needs in chemical, nuclear, biological, and high-explosives counterterrorism

Forensic Science Center

Created in 1991, the Forensic Science Center (FSC) has established a nationally recognized capability to support national-security-related programs at the Laboratory as well as at other national sponsors. Working directly with Livermore's Nonproliferation, Arms Control, and International Security Directorate, FSC combines state-of-the-art science and technology with expertise in chemical, nuclear, biological, and high-explosives forensic science to support national security. FSC also collaborates with and supports federal agencies that protect the United States by applying forensic technology to help defeat terrorists or interdict dangerous materials.

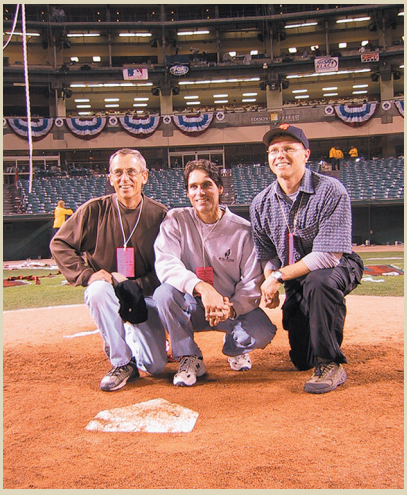


Figure 1. These FSC scientists helped plan an effective forensic response to the potential use of weapons of mass destruction at the 2002 World Series.

In addition to playing a strong programmatic role, FSC conducts cutting-edge research in the areas of analytical science and instrument development, nuclear forensic analysis, and the synthesis of new molecular and tailored nanostructured materials. We also encourage our scientists to maintain an active research presence in peer-reviewed publications, scientific meetings, and professional societies.

CMS Research Theme Alignment

The work at FSC supports two CMS research themes: *science in support of national objectives at the intersection of chemistry, materials science, and biology* and *applied nuclear science for human health and national security.*

Major Accomplishments in 2002

After successfully completing the 11th and 12th Organization for the Prohibition of Chemical Weapons (OPCW) round-robin tests, FSC became only the second designated U.S. support laboratory for the Chemical Warfare Convention. The two-week tests involved identifying chemical-warfare agents in diverse and complicated sample matrices; these matrices included a number of "red herring" compounds that masked the true targets. The FSC team passed both tests in 2002, capping a three-year effort for OPCW certification, which was awarded in February 2003.

The Laboratory also contributes expert members to the OPCW data-validation group. This group works to continuously evolve the high-quality mass spectrometry, infrared, and nuclear magnetic resonance techniques that are used to collect data for chemical-warfare databases. In addition, FSC was recently requested to participate in the first OPCW off-site sampling exercise to evaluate shipping and analysis protocols.

At the national level, FSC scientists are helping to plan an effective forensic response to the potential use of weapons of mass destruction at domestic events, such as the 2002 World Series (Figure 1). For example, FSC scientists serve as members in the FBI's Chemical Terrorism Scientific Working Group and are leading a nascent FBI Scientific Working Group that is focused on radioactively contaminated evidence. FSC staff members are internationally recognized experts in both areas.

FSC researchers also commercialized some of their instrumentation and technology in 2002. For example, FSC staff scientists reduced the standard 114-kilogram laboratory gas chromatograph/mass spectrometer

(GC/MS) to fit inside a wheeled suitcase without sacrificing specificity or sensitivity. Our portable GC/MS is completely self-contained and comprises a power generator, vacuum pumps, a carrier-gas system, and a laptop computer.

In ongoing studies, FSC scientists continued to produce advancements in newly tailored nanostructured materials to collect and detect targeted chemical signatures, conduct laser-ablation mass spectrometry experiments, and perform extraordinary sample analyses for a diverse group of agencies.

State-of-the-Art Technologies

Developing new tools for intelligence, law-enforcement, homeland-security, and health professionals at remote field locations is a particular area of excellence at FSC. These compact, battery-operated instruments provide mobile chemistry laboratories that greatly expedite data acquisition and decision making.

Thin-Layer Chromatography Kits

FSC scientists have miniaturized and modernized thin-layer chromatography (TLC), a historic chemical procedure that identifies compounds belonging to the same general class of analytes with high specificity and sensitivity. Suitable for field use, a complete TLC kit fits inside a suitcase and weighs about 23 kilograms. A single kit can be used to analyze two sets of samples simultaneously, with each set containing about 10 samples. The analysis of a single sample typically takes 15 to 45 minutes to complete, depending on the type of sample.

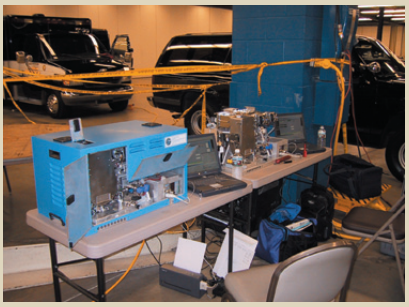


Figure 2. This portable gas chromatograph/mass spectrometer is used to analyze unknown chemicals in the field.

Mini Gas Chromatograph/Mass Spectrometer

The Mini GC/MS (Figure 2) is a robust, reliable, and field-deployable instrument. With an ability to analyze samples at sensitivities of parts per billion within 15 to 40 minutes, the portable GC/MS can be used during homeland-defense activities, incident response, and law-enforcement investigations. For example, the instrument can precisely identify compounds that indicate the production of chemical-warfare agents and illicit drugs. The Mini GC/MS has been deployed worldwide and is currently being manufactured under licenses to Constellation Technologies, Inc. and Kobelco Ltd., Japan.

Laser-Ablation Mass Spectroscopy

Most solid objects do not have a significant vapor pressure, so FSC scientists are developing laser-ablation mass spectroscopy to directly analyze solid material. The primary strength of laser-ablation mass spectrometry is that it greatly reduces the time required for sample pretreatment. The technique combines a Nd:YAG laser to vaporize extremely small amounts of material, an ion trap and time-of-flight mass spectrometer to analyze particles, and a high-magnification, charged-coupled device microscope to view and manipulate target species in real time. FSC scientists can use this method to analyze and rapidly identify suspect signature species of various activities.

Solid-Phase Microextraction

Solid-phase microextraction (SPME) uses coated optical fibers as a "chemical dipstick" for the safe and efficient sampling of a myriad of questionable specimens. This collection technique requires no solvents, sample workup, or additional equip-ment and does not generate any hazardous waste. To improve the robustness of the fibers, we developed portable kits of rugged, aluminum transport tubes; each tube secures one syringe and fiber, and each kit contains five tubes. The hermetically sealed tubes prevent cross-contamination and support chain-of-custody requirements.

The FBI and other agencies use SPME field kits to collect chemical-warfare agents safely and rapidly, to detect drugs, and to investigate arson. A pocket-sized version is currently being developed, and both kits are being licensed to industry for sale to government agencies. SPME sampling is also used in the Stockpile Stewardship Program to safely monitor nuclear-weapon warheads.

Future Goals

FSC is poised to be an integral component of the national response network for domestic events involving weapons of mass destruction and conventional terrorism. Working with the Department of Homeland Security, the FBI, the Department of Energy, and pertinent intelligence agencies, FSC is strengthening programmatic connections that will use FSC and other unique resources in CMS and the rest of the Laboratory.

FSC scientists will also continue to expand their basic science capabilities in the research areas of analytical science and instrument development, nuclear forensic analysis, and new molecular and nanostructured materials synthesis. These three scientific thrust areas efficiently overlap our customers' long-term needs and should position FSC to provide critical leadership for new programmatic areas in the future.

Author
G. Fox

Glenn T. Seaborg Institute

The Glenn T. Seaborg Institute was established in 1991 to foster research in fundamental and applied nuclear science and technology. The institute was named in honor of Dr. Seaborg to recognize his enormous contributions to the field of nuclear science and to science education, as well as his many years of service to the nation and to the University of California.

The Seaborg Institute emphasizes the training of future generations of nuclear scientists. Our Nuclear Science Internship Program (NSIP), which is sponsored by the Department of Energy, provides nuclear science students with individual mentors, who then train the students in nuclear and analytical chemistry methods.

CMS Research Theme Alignment

In alignment with the CMS research theme of *applied nuclear science for human health and national security*, the nuclear and bionuclear science efforts at the Seaborg Institute focus on (1) supporting the safety and reliability of the nation's nuclear-weapons stockpile, (2) helping to counter terrorism and deter the proliferation of nuclear materials, (3) applying radiation science to improve human health, (4) tackling environmental problems affecting drinking-water safety and nuclear-waste cleanup, and (5) enhancing public understanding and student involvement in nuclear science. These efforts contribute to national security, while also promoting a clean environment and aiding the detection and treatment of disease.

Our research supports the national-security efforts of the Stockpile Stewardship Program. Our work also helps to stem the proliferation of nuclear weapons and materials by developing advanced detection techniques that use atomic mass and radioactive signatures to discover and identify radioactive and nuclear-proliferation materials.

Major Accomplishments in 2002

Our research measures isotopic compositions, radioactive emissions, and radiochemical properties. This expertise is applied to the following:

- Discovering the physical and chemical properties of nature's heaviest elements.
- Mapping the presence of radioisotopes and radiation dose in biological systems (e.g., the human body) and the biosphere.
- Imaging life processes and pharmaceutical kinetics at scales ranging from the whole body to dimensions smaller than a cell.
- Fingerprinting the history of objects, ranging from meteorites to nuclear weapons materials.

Highlights of our accomplishments in 2002 follow.

Bionuclear Science

- Synthesized our first synthetic high-affinity ligands (SHALs) that are targeted against non-Hodgkin's lymphoma and botulism toxin.
- Tested our SHALs against non-Hodgkin's lymphoma and found

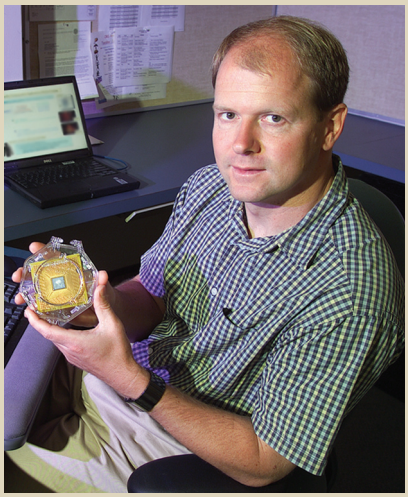


Figure 1. A component of the Compton imager, a device being developed by the Glenn T. Seaborg Institute to image cancer and help detect the unauthorized transport of radioactive materials.

that our prototype SHAL inhibited binding of the Lym-1 antibody.

- Obtained our first secondary-ion mass spectrometry (SIMS) images for an yttrium-labeled 13 kDalton decapeptide distribution in a mouse kidney.

- Demonstrated the first prototype of an advanced gamma-ray imaging systems study and concluded that a semiconductor-based hybrid Compton imaging system provides the highest sensitivities for cancer imaging (Figure 1).

- Demonstrated the accuracy of the MINERVA system for internal radiation sources. MINERVA is designed to calculate patient-specific radiation dose estimates by using computed tomography to describe patient anatomy in combination with a user-defined 3-D source.

Nuclear Science

- Continued investigating the "island of stability" of superheavy elements by bombarding californium-249 with calcium-48 ions at the U400 cyclotron.

- Detected two events that may be attributed to the formation and decay of an element 118 isotope.

- Developed a combined experimental and theoretical approach to calculate thermodynamic behavior for the plutonium–gallium–iron ternary phase diagram, which is needed to understand phase behavior in stockpile materials.

- Began a program to address groundwater contamination at the Semipalatinsk Test Site in eastern Kazakhstan, where more than 400 nuclear tests were conducted from 1949 to 1989.

- Initiated a cooperative effort with several states of the Persian Gulf to prepare regional governments to respond to the threat of nuclear, biological, and chemical weapons of mass destruction.

- Continued investigations to determine the absolute age of the oldest objects in the solar system.

- Demonstrated that primitive meteorites formed about 30 million years before Earth.

Education

- Hosted 22 graduate and undergraduate students in NSIP (Figure 2). The students conducted nuclear science research projects and attended lectures given by leading nuclear scientists.

- Awarded the first Darleane Hoffman and Gerald Wasserburg fellowships to promote excellence in nuclear science at the graduate level.

State-of-the-Art Technologies

We recently installed a new Cameca NanoSIMS ion microprobe, which provides a 40 times improvement in lateral resolution and a 10 times increase in sensitivity. We are also leveraging programmatic investments in Compton imaging to design a diagnostic system that will improve the sensitivity and accuracy of radioisotope imaging agents. Our system will also demonstrate the medical value of modern Compton imaging by detecting 1- to 2-millimeter breast cancer lesions.

We are characterizing the two-detector high-purity germanium (HPGe) detector system to nuclear-medicine imaging specifications. We are also assembling the first high-purity silicon (HPSi) component and are improving detector sensitivity through digital signal processing. In the future, we plan to assemble the first HPSi–HPGe hybrid Compton imager.

Future Goals

Our goals are to enhance the impact of nuclear and bionuclear science on important national problems such as homeland security, health, and the environment. Together with national-security organizations, we will apply the science of isotopic signatures to identify illicit manufacturers of biological and nuclear weapons. We will also apply nuclear and bionuclear science to minimize the effects of nuclear and radiological weapons.

In addition, we will continue our quest to study nature's newest elements, as well as our efforts to improve the accuracy and effectiveness of molecular targeted radioisotope therapy for advanced cancer.

Author
C. Hartmann Siantar

Figure 2. Students from the 2002 Nuclear Science Internship Program, which provides the next generation of nuclear scientists with mentors and career support.

Dynamic Teams:

An institute that maintains cutting-edge materials research through a collaborative effort between the Laboratory and the nation's universities

Materials Research Institute

The Materials Research Institute (MRI) facilitates strategic collaborations between university researchers and the next generation of interdisciplinary Laboratory leaders through immersive research experiences. MRI hosts a number of activities that bring students and other guests into the Laboratory for both short- and long-term visits. During 2002, the Second Annual Summer Institute for Computational Materials Science and Chemistry hosted 11 students (Figure 1); further expansion to 15 students is underway for 2003.

CMS Research Theme Alignment

The Laboratory is recognized as the world leader for its research in materials under extreme conditions, which is in alignment with the CMS research theme of *materials properties and performance under extreme conditions*. In addition, nanoscience and technology has been targeted by the White House through the National Nanotechnology Initiative as a strategic investment area for the United States. Therefore, MRI focuses on these theme areas to support future growth.

Major Accomplishments in 2002

MRI sponsors workshops so that Laboratory scientists are introduced to the spectrum of activities that exist within the Laboratory and elsewhere. The MRI staff is also responsible for preparing a targeted portfolio of projects for the Laboratory Directed Research and Development (LDRD) program; each of these projects requires collaboration with university researchers. For the last several years, MRI has directed this portfolio into cutting-edge nanoscience projects. Highlights include the following:

- **Probing the properties of cells and cell surfaces with the atomic force microscope (AFM)**. A single receptor molecule bound to the tip of an AFM cantilever can now be used to map the locations of ligands bound on solid surfaces, opening the door for new recognition-mapping methods.

This project contributes to LLNL's national-security mission by creating a method for measuring the real-time response of individual living cells to a range of perturbations, from chemical and thermal changes in the cells' environment to infection or poisoning by bacteria and toxins (e.g., those manifested by biological- and chemical-warfare agents). Our technique will provide a new, nondestructive means to detect changes in cell-membrane properties at the nanoscale.

The experimental data in Figure 2 show the results of a new variation of recognition microscopy that was developed as part of this project. Both the target ligand and the targeting molecule on the AFM tip are tethered on polymer chains so that the ligand and molecule can reorient for optimum binding and so that nonspecific binding events can be distinguished from the specific events that are of primary interest. This first step will pave the way for using our new recognition-mapping method in a living cell.

This project combines computational modeling with experiments to help us understand the complex response produced by the

Figure 1. Student participants and their hosts at the Second Annual Summer Institute for Computational Materials Science, which was held in 2002.

interaction of an AFM cantilever with a living cell. By using experimentally determined force as a function of distance curves, we have developed an initial continuum model of the living cell. This model, which is undergoing further iterations as our experiments evolve, is essential for helping us to deconvolute the various processes that are observed on the surface of a living cell.

- **Using nanoparticles to improve magnetostrictive elastomer composites**. Magnetostrictive materials have a broad range of applications, ranging from smart airplane wings to microelectromechanical systems for medical applications. In many cases, improvements in material performance have led to new possibilities for the use of magnetostrictive materials.

  At MRI, we have been exploring the possibility of dramatically reducing the magnitude of the fields needed to actuate a magnetostrictive device by creating "core-shell" systems. Nanoparticles of a magnetostrictive material would first be coated with a different magnetic-layer core shell. These particles could then be incorporated into elastomer composites to produce useful magnetostrictive devices.

- **Developing ultrasensitive high-speed biological assays based on 2-D flow-cell detection of single molecules**. We are developing a device that combines microfluidics and total-internal-reflection (TIR) microscopy to provide a generalized biological assay with better-than-femtomolar detection limits. This device will have 10^3 to 10^4 times greater throughput than previous one-dimensional microstream devices, enabling immuno- and DNA assays at ultralow concentrations to be performed in short time periods (less than 10 minutes).

  Once developed, the planar microchannel/TIR microscope will be used to demonstrate ultrasensitive assays of biological species for pathogen-detection applications, which are relevant to homeland security. This new technology will also impact health care by advancing medical research, drug discovery, and basic scientific research.

During 2002, we constructed a dual-channel TIR imaging system that demonstrates single-fluorescent-molecule detection limits. We also successfully fabricated microfluidic devices with dimensions consistent with our proposed device. The completed system was tested and optimized using fluorescent molecules immobilized on glass substrates and dye-loaded microspheres flowing in the microfluidic channel.

We also submitted a patent application for the planar microchannel/imaging system. In 2003, we plan to continue optimizing the planar microchannel/imaging system and expect to demonstrate the analysis of biomolecular species at ultralow (femtomolar) levels.

Future Goals

Our goal is to help Livermore stay on the cutting edge of materials research activities that have promise for future mission relevance. We plan to achieve this goal by supporting areas such as nanofabrication and nanoscience to fabricate sensors and targets for the National Ignition Facility.

In addition, we intend to strengthen our current nanomechanics team by partnering with Laboratory scientists and establishing strategic university collaborations. We will also use funds from LDRD and the University Collaborative Research Program to recruit and support the expanded nanomechanics/sensor-modeling team.

Authors

M. McElfresh, D. Brosnan, and T. Ratto

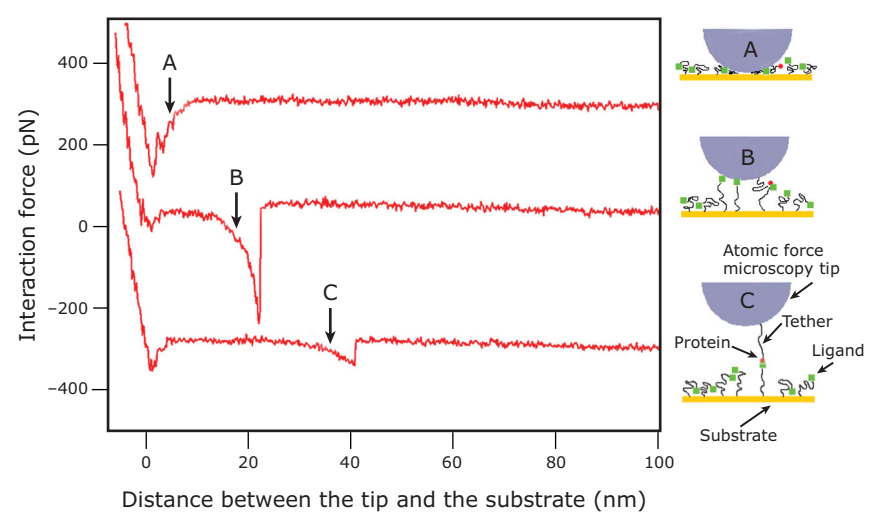


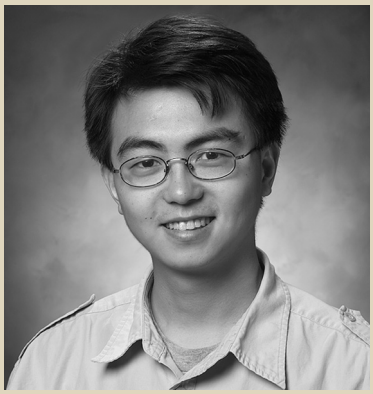
Figure 2. Experimental atomic force microscopy (AFM) retraction curves (left) and schematics (right) showing the interactions between an AFM tip and a substrate at three characteristic distances: A, nonspecific tip–substrate interactions (less than 10 nanometers); B, nonspecific tip–ligand interactions (between 10 to 30 nanometers); and C, specific protein–ligand interactions (between 30 to 40 nanometers). The zero point on the *x*-axis denotes the point of contact between the tip and the substrate. In addition, the force curves of A and C have been rescaled along the *y*-axis.

Awards and Recognition in 2002


Tomas Diaz de la Rubia


Randy Simpson


Olgica Bakajin


Wei Cai

Headlines

CMS senior scientist **Brian Andresen** received two awards, including a Distinguished Service Award for forensic science work conducted with the assistance of analytical chemist **Armando Alcaraz**. This work helped police in Glendale, California, solve the Efren Saldivar murder case.

Tomas Diaz de la Rubia and **John Elmer** received special recognition from their respective professional societies during 2002:

- **Tomas Diaz de la Rubia** was named a Fellow of the American Physical Society (APS). No more than one-half of one percent of the APS membership is elected to the status of Fellow. Tomas was nominated by the Computational Physics Division of APS "for his contributions to multiscale modeling of materials and seminal work on defect processes in solids under irradiation or high-strain-rate conditions."
- **John Elmer** received the A. F. Davis Silver Medal Award from the American Welding Society (AWS) for his work, "An enhanced Faraday cup for rapid determination of power density distribution in electron beams." John has received other AWS awards, including being named as a Fellow, for his work in metallurgy and the kinetics of weld phase transitions.

Chemist **Leonard Gray** received the 2002 Glenn T. Seaborg Actinide Separation Medal for his "outstanding accomplishment and meritorious achievement in actinide separations science."

Jon Maienschein and CMS scientists and administrators from the Energetic Materials Center hosted the 12th International Detonation Symposium, a major event in the field of high explosives and energetic materials, in August 2002 in San Diego.

CMS senior scientist **Randy Simpson** was honored with a Weapons Recognition of Excellence Award from the National Nuclear Security Administration for his leadership of high-explosives development and analysis activities.

A team that included **Chris Walton** of the Materials Science and Technology Division (MSTD) received the prestigious R&D 100 Award for a "production-scale, thin-film coating tool for next-generation semiconductor technology."

Lawrence Fellows

After undergoing a rigorous selection process, postdoctoral fellows in the Lawrence Livermore Fellowship Program, known as Lawrence Fellows, can choose the group in which they want to work. We are proud that the following Lawrence Fellows have selected research projects within the CMS Directorate.

Olgica Bakajin, Ph.D. in physics from Princeton University. She is using microfabrication to manipulate biological fluids and is studying the behavior of biological molecules in micro- and nanochannels under hydrodynamic flow and electric fields.

Wei Cai, Ph.D. in nuclear engineering from the Massachusetts Institute of Technology (MIT). Wei is identifying atomic unit mechanisms in dislocation mobility and is working on a new massively parallel computer code for modeling dislocation dynamics.

Julio Camarero-Palao, Ph.D. in organic chemistry from the University of Barcelona. Julio's research focuses on chemoselective ligation approaches, which involve linking polypeptide building blocks to produce target protein sequences.

Sergei Kucheyev, Ph.D. in physical sciences from the Australian National University. Sergei's research interests include ion- and laser-beam-induced modification of solids and the deformation behavior of semiconductors.

Certification

The Forensic Science Center (FSC) was certified by the Organization for the Prohibition of Chemical Weapons (OPCW) in The Hague, the Netherlands, as one of two approved U.S. laboratories for the analysis of chemical-warfare agents. The certification, which followed an initial selection by the U.S. Department of State and rigorous trials and audits by OPCW, is a reflection of the superb analytical and synthetic chemistry being conducted by CMS scientists in FSC.

Patents and Invention Disclosures

CMS scientists and engineers participated in groundbreaking research that resulted in at least 19 invention disclosures, 25 patent applications, and 8 issued patents in 2002. Of these, 13 invention disclosures, 22 patent applications, and 6 issued patents were funded by the CMS Directorate.

Editorships

Many CMS scientists play important roles in their respective professional societies, with about 15 CMS researchers serving as editors of technical journals. These scientists, some of whom are listed below, provide a valuable connection between CMS and researchers at universities, other national laboratories, and important industries.

- **Trish Baisden**, Editor of *Radiochimica Acta*
- **Vasily Bulatov**, Editorial Board of *Modeling and Simulations in Materials Science and Engineering*
- **David Eaglesham**, Editorial Board of the *Materials Research Society Bulletin*
- **Tai-Gang Nieh**, Editorial Board of *Intermetallics*
- **Randy Simpson**, Coeditor of *Propellants, Explosives, Pyrotechnics*
- **Patrice Turchi**, Editorial Board of *Materials Transactions*
- **Charles Westbrook**, Editorial Board of *Combustion and Flame* and *International Journal of Chemical Kinetics*

Scientific Publications

The number of scientific publications by CMS researchers increased from about 220 refereed articles in 2001 to more than 280 in 2002. The number of publications in the most prestigious journals (e.g., *Nature*, *Science*, and *Physical Review Letters*) also increased. This level of productivity increased at a higher rate than the number of CMS scientists because the directorate has been giving more attention to publications and because publications are viewed as a critical part of career development by our postdoctoral researchers and other recently hired scientists. Papers by CMS researchers have also appeared as featured articles in various journals, including the following in 2002:

- "Evaluation of silica–water surface chemistry using NMR spectroscopy" by Susan Carroll, **Robert Maxwell**, William Bourcier, Sue Martin, and **Suzanne Hulsey** (*Geochimica et Cosmochimica Acta* [2002] *66,* 913). This article was cited as one of the journal's 25 most downloaded articles of 2002.
- "Prediction of extended aromaticity for a novel $C_{48}N_{12}$ aza-fullerene structure" by **M. Riad Manaa**, **David Sprehn**, and **Heather Ichord** (*Journal of the American Chemical Society* [2002] *124,* 13990). This article was listed as a Hot Article on the Web site of the American Chemical Society. (David Sprehn was a high school summer student in CMS, and Heather Ichord was an undergraduate summer student sponsored by CMS and the Laboratory's Military Academic Research Associates Program.)

This increased visibility trend of CMS research is continuing in 2003, with several papers being cited extensively and featured by leading journals.

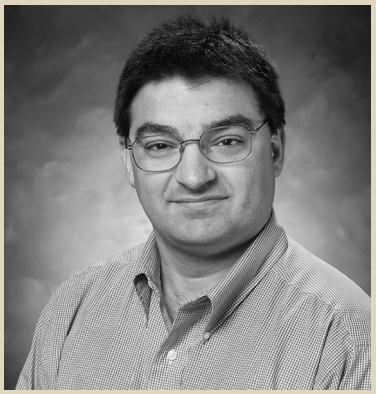
University Collaborations

The research activities of CMS members frequently include technical interactions with leading groups and individuals at universities in the United States and other countries. Most interactions are informal and are based on common technical interests and research. Many of these collaborations result in publications, and an examination of CMS publications in 2002 shows that such interactions are extremely productive and important to CMS.

A few interactions with university research programs have been identified as particularly desirable and valuable, leading CMS to provide funding to these programs to facilitate interactions (e.g., by granting graduate students and faculty special access to the Laboratory). There were three such active collaborations in 2002:

- Dr. Roberto Car of Princeton University partnered with **Tomas Diaz de la Rubia**, **Lou Terminello**, and **Vasily Bulatov** from the Computational Materials Science Group in MSTD to investigate methods in computational materials science.
- Dr. Mildred Dresselhaus of MIT partnered with **Joe Satcher** from the Chemical Synthesis Group in the Chemistry and Chemical Engineering Division (CChED) on the production and characterization of aerogels.
- Dr. Dudley Herschbach of Harvard University partnered with **Carl Melius** of CChED on research focusing on extreme chemistry at high temperatures and pressures.

Author
C. Westbrook


Julio Camarero-Palao


Trish Baisden


Charles Westbrook

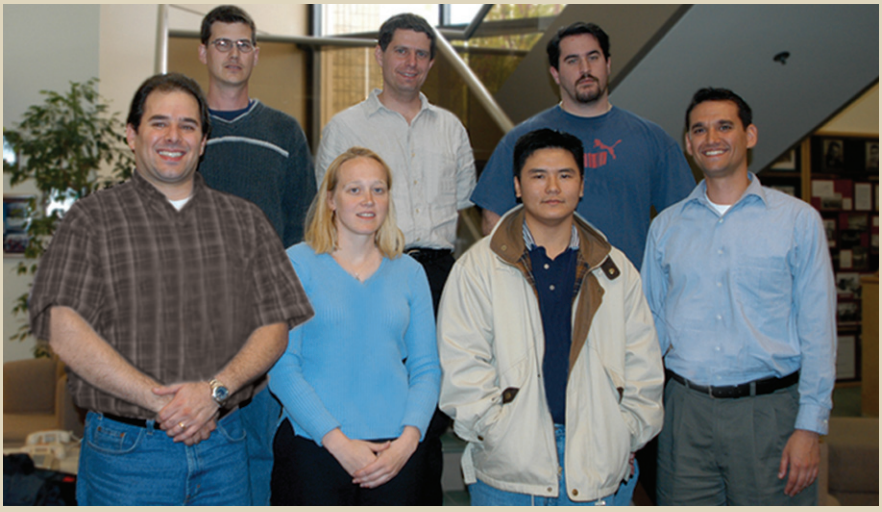

Robert Maxwell

CMS Postdoctoral Program

During the past year, CMS has supported an average of 10 postdoctoral researchers through the CMS Postdoctoral Program, which is directed by **Tom Arsenlis**, and has provided them with mentors across all three divisions. These postdoctoral employees, who have become a very important part of CMS over the past few years, are selected according to several criteria (e.g., academic excellence and high-quality Ph.D. thesis research) and receive both programmatic and directorate funding.

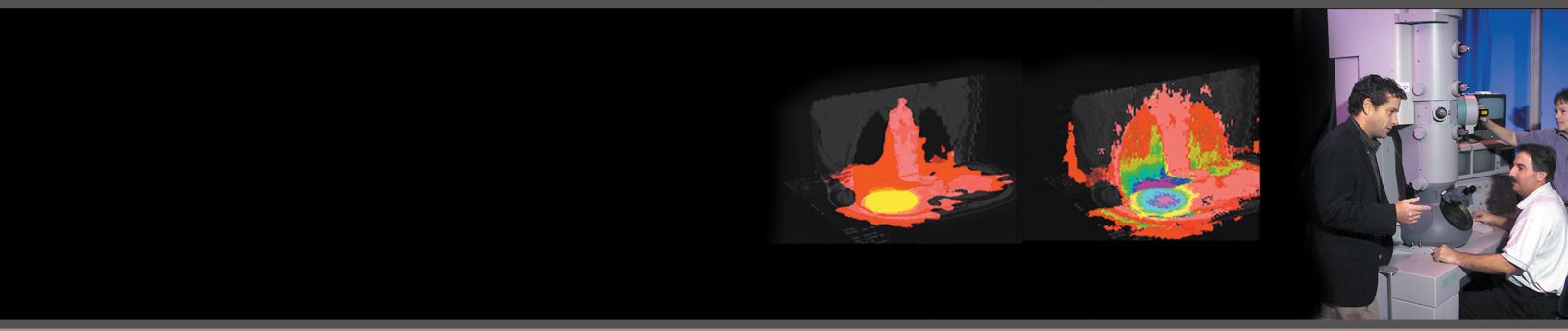
CMS postdoctoral researchers contribute to basic research efforts and programmatic projects. They also help develop new research areas and reinforce existing areas in coordination with the long-term science and technology planning process in CMS. The following is a list of current researchers in the CMS postdoctoral program (A complete list of all postdoctoral researchers in the CMS Directorate can be found at http://www-cms.llnl.gov/PostDocs/pdfellows.html):

- **Barry Cheung**, Ph.D. in physical chemistry from Harvard University. Barry is working with **Jim De Yoreo** in the BioSecurity and Nanoscience Laboratory (BSNL) on the assembly of ordered 2-D virus and protein arrays.
- **Jonathan Crowhurst**, Ph.D. in physics from the University of the Witwatersrand, Johannesburg, South Africa. Jonathan is working with **Joe Zaug** of the Chemistry and Chemical Engineering Division (CCheD) on experiments at high pressure and temperature to determine the elastic properties of metals under ultrahigh static pressure.
- **David Fergenson**, Ph.D. in chemistry from the University of California (UC) at Riverside. David is part of a BSNL team that is developing a method of biological mass spectrometry capable of analyzing individual airborne microorganisms in milliseconds.
- **Brad Hart**, Ph.D. in synthetic organic chemistry from UC Irvine. Brad is working with **Glenn Fox** in the Forensic Science Center to develop materials for molecular recognition.



Researchers in the CMS Postdoctoral Program (counterclockwise from top right: Rob Meulenberg, Bryan Reed, Brad Hart, Luiz Zepeda-Ruiz, Julie Herberg, and Will Kuo) and Tom Arsenlis (bottom far right), director of the program.

- **Julie Herberg**, Ph.D. in physics from Washington University in St. Louis. Julie is working with **Bob Maxwell** in the Laboratory's Center for National Security Applications of Magnetic Resonance. Julie is helping to develop a portable microcoil nuclear magnetic resonance system and is characterizing the structure and dynamics of a variety of materials, including bacterial spores, proteins in cells, and hydrogen in metal hydrides.
- **Will Kuo**, Ph.D. in physical chemistry from UC Irvine. Will is working with **Chris Mundy** of CChED to apply computational chemistry to aerosol and structural biology problems.
- **Rob Meulenberg**, Ph.D. from UC Santa Barbara. Rob is working with **Tony van Buuren** in the Materials Science and Technology Division (MSTD) on experimental studies of the electronic structure of silicon and germanium nanoparticles.
- **Lucian Mihailescu**, Ph.D. in physics from the University of Bonn in Germany. Lucian is working on advanced gamma-ray imagers with groups in the CMS and Physics and Advanced Technologies directorates.
- **Tim Ratto**, Ph.D. in biophysics from UC Davis. Tim is working with **Mike McElfresh** of the Materials Research Institute to use force spectroscopy to localize and measure protein–ligand interactions on cell and cell-like surfaces.
- **Bryan Reed**, Ph.D. in applied physics from Cornell University. Bryan is working with **Mukul Kumar** of MSTD on shock physics and grain-boundary thermodynamics.
- **Luiz Zepeda-Ruiz**, Ph.D. in chemical engineering from UC Santa Barbara. Luiz is working with **Maria Bartelt** of MSTD in computational and theoretical studies of the growth of potassium diphosphate crystals for National Ignition Facility optics.



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